Improving the yield strength of an antibacterial 304Cu austenitic stainless steel by the reversion treatment

Mahesh C. Somani\textsuperscript{a}, Matias Jaskari\textsuperscript{a}, Saeed Sadeghpour\textsuperscript{a}, Chengyang Hu\textsuperscript{b}, R. Devesh K. Misra\textsuperscript{b}, Tun Tun Nyo\textsuperscript{a}, Chung Yang\textsuperscript{c} and L. Pentti Karjalainen\textsuperscript{a}

\textsuperscript{a}Centre for Advanced Steels Research, University of Oulu, 90014 Oulu, Finland
\textsuperscript{b}Laboratory for Excellence in Advanced Steel Research, Department of Metallurgical, Materials and Biomedical Engineering, University of Texas at El Paso, TX 79968, USA
\textsuperscript{c}Institute of Metal Research, Chinese Academy of Science, Shenyang, 110016, China

Abstract

As an implant material, Cu-bearing austenitic stainless steels can possess the antibacterial property, but their mechanical strength is low. In order to improve the yield strength of a 304Cu (17%Cr-7%Ni-3%Cu) alloy through substantial grain refinement, a research investigation has been taken up to conduct the reversion annealing treatment comprising a heavy (71%) cold rolling reduction followed by annealing at various temperatures (650–950 °C) and durations (1–5400 s). The microstructure evolution was examined by electron backscatter diffraction and further characterized by magnetic measurements, and mechanical properties were determined by tensile and hardness testing. The precipitation of Cu was confirmed by transmission electron microscopy. It was found that the reversion of deformation-induced martensite to austenite took place by the shear mechanism, followed by subgrain formation and continuous recrystallization resulting in quite non-uniform grain size distribution. The finest reversed grains were around 0.6 µm in size, but also much larger austenite grains and a small fraction of unreversed martensite existed in the final structure despite annealing at least up to 800 °C. Coherent Cu particles were observed after aging for 1.5 h at 700 and 650 °C, while the yield strength could be improved to 507 and 791 MPa,
respectively, i.e. by ~2–3 times that of the annealed steel. The ductility of the steel remains still high, the fracture elongation being 36%.

*Keywords:* 304Cu austenitic stainless steel; reversion treatment; grain size; precipitation; yield strength; antibacterial property

1. Introduction

Austenitic Cr-Ni stainless steels have a wide variety of applications in food processing, infrastructure, transportation, medical and other fields owing to their superior corrosion resistance and workability. They are, for instance, commonly used orthopedic implant materials having favorable rigidity, formability, corrosion resistance, and biocompatibility [1,2]. The long-term antibacterial feature is an additional property desired for an implant material. Copper has been shown to be a multifunctional metallic element with various antimicrobial and anti-inflammatory activities. It has, therefore, been incorporated into a wide range of materials to improve their antibacterial property [1,2]. Also common austenitic stainless steels, such as AISI 304/304L and AISI 316L, when alloyed with about 3%Cu (hereinafter, concentrations are in wt.%) have been found to demonstrate antibacterial properties [3–5], similarly as AISI 317L-4.5Cu [2,6], as well as ferritic stainless steel(s) [7] and a maraging steel [8]. Overall, Cu-bearing antibacterial austenitic stainless steels, developed as a new class of structural and functional integrated materials, have attracted much attention as a potential biomaterial for implant devices during recent two decades, e.g. [1,2,4,6,9].
However, the strength level of an annealed austenitic stainless steel is quite moderate, for instance the yield strength (YS) is typically around 250–270 MPa and the ultimate tensile strength (UTS) 540–700 MPa for AISI 304 and 316 type steels [3,4,10]. Cu alloying results in only marginal solid solution strengthening, but the UTS eventually declines with Cu alloying limited to < 2.5%, as a consequence of the lower strain hardening ability of the austenite [4,10]. This is obviously a result from the fact that Cu is one of the elements that increases the stacking fault energy (SFE) of the austenitic stainless steel and stabilizes the austenitic structure [10,11]. The UTS increases slightly with higher Cu contents, but stays practically at 630 MPa level even after alloying with 5.5% Cu [4]. Further, it has been clarified that the Cu content should not exceed ~3.5% to ensure that a balance exists among the formability, corrosion resistance and antibacterial properties [4].

Xi et al. [3] found that in a 316L type steel with varying contents of Cu at 0, 2.5 and 3.5%, the YS following the solution treatment was almost constant, whereas the aging treatment increased the YS due to formation of tiny Cu-rich precipitates. Still, the properties (YS 257 MPa and UTS 543 MPa) achieved in the 316L-3.5Cu steel (aged at 700 °C for 6 h), were very moderate.

Very recently Luo et al. [12] investigated the influence of Cu concentration (2.2% and 2.98%), austenite solid solution temperature and aging temperature, on the strength of type 304Cu antibacterial steel. A combination of optimal strength and best antibacterial effect were obtained through a treatment comprising annealing at 1050°C for 30 min, followed by quenching to room temperature (RT) and aging at 650 °C-90 min, while the hardness also reached a maximum level of 150–160 HV. However, this hardness corresponds to a very moderate strength level only [3].
Thus, a higher strength, particularly a high YS, is desired. The reversion treatment includes a heavy deformation stage to transform the austenite to deformation-induced martensite (DIM) followed by a short annealing stage, whereby the martensite reverses back to austenite. The process has been known to be very efficient to refine the grain size (GS) in metastable austenitic stainless steels down to micrometer or even nanometer range, which results in improved YS and fatigue resistance, e.g. [12]. Due to the high stability of austenite in the 304/304L type steel, a high cold rolling reduction or rolling at subzero or cryogenic temperatures is quintessential for optimal results [13,14]. Anyhow, in numerous studies, annealing of cold rolled 304 steel at 700–800 °C for various durations has resulted in enhanced tensile properties in a wide range: YS 540–1120 MPa, UTS 850–1440 MPa, and total elongation (TE) 44–12% [3], see a recent review [15]. Thus, it can be argued that the reversion treatment can provide a YS level about 3–4 times higher than that of the conventional 304/304L steel, and still with good ductility.

To the best of authors’ knowledge nobody has applied the reversion treatment intentionally to an antibacterial steel until very recently at the authors’ laboratories [16], even though there are few investigations on the reversion of 2%Cu bearing Cr-Ni steels. Lei et al. [17] have studied an Fe-0.06C-17Cr-6Ni-2Cu steel with nanostructure obtained by a reversion treatment, although the authors did not pay any attention to the presence of Cu element in the material. Very fine GS of below 300 nm was reported after 75% cold rolling reduction and subsequent reversion annealing. Consequently, the YS obtained was about 980 MPa and UTS 1100 MPa with total elongation (TE) 30%, whereas the steel in the coarse-grained condition had the YS of 290 MPa, UTS 750 MPa and TE 57%.
Shakhova et al. [18] have studied a S304H type (Fe–0.1C–0.12N–18.4Cr–7.85Ni–2.24Cu–0.5Nb) austenitic stainless steel. A very heavy caliber rolling reduction up to a total strain of 4 was applied to obtain 65% of DIM. The subsequent annealing at 500–700 °C (30–120 min) resulted in a transversal subgrain size of 50–170 nm. However, the elongation remained low, except when annealing at a temperature 700 °C or above, where after 2 h holding the YS was 1050 MPa, UTS 1160 MPa and a moderate TE of 9%. Also, Kisko et al. [19] have studied the reversion of an AISI 204Cu (Fe-0.08C-15Cr-9Mn-1Ni-1.7Cu) steel, but any influence of Cu alloying has not been highlighted. As an example, impressive tensile properties of the order of YS 899 MPa, UTS 1345 MPa and TE 51% were reported after cold rolling and annealing at 700 °C for 100 s.

Based on the previous successful results, the reversion treatment can be expected to be an efficient process also for the AISI 304Cu grade as regards the GS refinement and enhancement of strength properties are concerned, although the alloying with Cu is known to increase the SFE. This in turn would render the steel less metastable [10,11,20,21], thus decreasing the extent of DIM fraction formed in the cold rolling stage. Furthermore, it has been demonstrated for a 301LN steel that a highly refined GS is beneficial for medical applications because of the improvement of cell adherence on surfaces and enhanced tissue growth [22,23]. Therefore, in addition to enhanced strength, surface properties in respect of biocompatibility might also be improved due to the refined GS.

However, precipitation of Cu particles is inevitably necessary to obtain the desired antibacterial property for biomedical applications. According to some studies, an aging duration of 1–4 h at 800 °C is suitable for a significant amount of Cu precipitation to provide the antibacterial property
in 304Cu steel [4,9], but of late, aging times as short as 1.5 h at 650 °C [12] or 0.5 h at 750 °C [24] have been suggested for optimal processing. Anyhow, due to relatively long isothermal ageing times, one might be justly concerned about a risk of grain growth or other microstructural changes that could debilitate the advantage of the reversion treatment on the strength.

In the present study, in order to demonstrate the potential enhancement in the strength under conditions relevant to the antibacterial property, the reversion treatment was applied quite comprehensively to a 304L steel alloyed with 3.15% Cu in order to examine the microstructure evolution and GS refinement at various reversion temperatures and durations and their influence on tensile properties. Also, a practical cold rolling reduction of ~71% was applied to the experimental sheet. The reversion mechanism and interpretation of details of the reversed grain structure in a 304Cu steel, as formed from partially transformed martensitic structure at RT, seem to be unclear in spite of the above-mentioned studies. Hence, attention was paid on utilizing the electron backscatter diffraction (EBSD) technique to understand the microstructural evolution. The kinetics of Cu precipitation during the reversion annealing of deformed martensite to austenite has not been investigated earlier, so the presence of Cu precipitates was confirmed by transmission electron microscopy (TEM), but more details are the topic of another paper. The antibacterial property due to fine precipitation of Cu has not been tested here, but many previous studies vouch for it [1,3,4,6–9].

2. Experimental
The chemical composition of the experimental 304L austenitic stainless steel containing 3.15% Cu is listed in Table 1. The typical features of this steel composition are its low C content (0.023%
C) and high stability as estimated using the stability index, $M_{d30} = -11.2^\circ C$ (for GS ASTM #7), as given below [25]:

\[
M_{d30} (^\circ C) = 552-462(C+N)-9.2Si-8.1Mn-13.7Cr-29(Ni+Cu)-18.5Mo-68Nb-1.42(GS-8) \tag{1}
\]

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

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
<th>$M_{d30}(^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023</td>
<td>0.55</td>
<td>0.85</td>
<td>17.40</td>
<td>7.32</td>
<td>3.15</td>
<td>0.011</td>
<td>0.025</td>
<td>Balance</td>
<td>-11.16</td>
</tr>
</tbody>
</table>

The steel was made as a laboratory casting using standard melting practice. For cold rolling, the steel was received in the form of a hot rolled sheet, ~3.2 mm in thickness. The as-received steel sheet was cold rolled in a laboratory rolling mill to 0.93 mm thickness (~71% reduction) and subsequently annealed in a Gleeble 3800 simulator at various temperatures in the range 650–950 °C using isothermal holding times between 1–5400 s. For reversion treatment, the samples were heated at 200 °C/s to the annealing temperature, held for desired duration and then cooled at the same rate at least down to 300 °C. The initial grain size of the sample was estimated as 31±4 µm.

Specimens for the metallographic characterization were ground and polished according to standard metallographic practice. Microstructural characterization was performed using a Zeiss Ultra Plus field emission gun scanning electron microscope (FEG-SEM) equipped with an electron backscatter diffraction (EBSD) device. Samples for EBSD scans were first ground gently to 600 grit and then to avoid any DIM formation during the mechanical preparation electropolished with perchloric acid solution. The EBSD scans were performed using the accelerating voltage of 15 kV, the working distance of 11 mm; step size was varied according to magnification being between 0.2 and 0.08 µm. All EBSD scans were made in RD-TD plane, i.e. ¾ thickness from the top surface.
The analyses of EBSD measurements were carried out using an Oxford HKL acquisition and analysis software in order to characterize the grain structure, grain and sub-boundaries and various phases.

Examination of Cu precipitation was performed on a JEOL JEM-2200FS scanning/transmission electron microscope (STEM/TEM) operated at 200 kV. Specimens for TEM/STEM were first ground to a thickness of 80 μm and then prepared using twin-jet electropolishing at -10 °C using 23 V DC in an electrolyte consisting of perchloric acid, ethanol, butyl cellosolve and distilled water (Struers A2).

DIM fractions were determined by a Ferritescope (Helmut Fisher FMP 30) instrument. The readings obtained were multiplied by a factor 1.7 for α'-martensite fractions.

Mechanical properties of the cold-rolled and reversion annealed specimens were determined by tensile testing. Uniaxial tensile tests were conducted at room temperature using a Zwick Z100 machine on specimens, taken along rolling direction, with the gage dimensions of 15 × 5 × 1 mm at an initial strain rate of 0.008 s⁻¹ (according to standard EN ISO-10002-1). Generally, tests were repeated twice. The hardness tests were carried out by use of Vickers method with a 5 kg load.

3. Results

3.1. Cold rolling

Cold rolling in 13 passes (about 15% each) to the total reduction of 71% resulted in the DIM fraction of 80%, so that still a significant amount of deformed austenite (DA) was retained. Fig. 1
shows the evolution of the DIM fraction during cold rolling. A gradual increase of martensite also means that inevitably some of DIM becomes deformed only slightly, for instance the half of martensite was deformed to a 30% reduction at the maximum.

3.2. Reversed microstructures

As the microstructure after cold rolling consisted of two phases, viz., DIM, i.e. $\alpha'$-martensite with varying degree of deformation, and deformed DA with $\sim71\%$ reduction, these two phases ought to behave differently during the reversion annealing treatment and inevitably results in variable microstructural features, which are visibly discernible especially for samples annealed at low temperatures.
We begin the description of microstructures from more simple structures obtained at high annealing temperatures and continue towards low-temperature annealing structures, the latter being more complex but providing better strength properties. Fig. 2 displays the microstructure after annealing for 1 s at 900 °C (annealing at 950 °C resulted in more or less similar but still coarser structure, not shown here), as observed by EBSD. The structure is fully austenitic, and the GS is slightly non-homogeneous consisting essentially of fine grains of few microns in size and larger grains up to 10 µm (Fig. 2a). (The GS distribution is shown later in section 3.4.) This inhomogeneity is due to a mixture of reversion-refined fine grains formed from DIM and recrystallized grains formed from DA, as reported in many papers, e.g. [26,27]. The orientation image microscopy (OIM) map (Fig. 2b) reveals that the grains appear in different colors, i.e. they have random orientation, although green colored {110} <hkl> grains seem to be most prominent.

At 850 °C-1 s hold, the local inhomogeneity in GS was even more pronounced due to lesser grain growth than that occurred at 900 °C (Fig. 3a). At this temperature, few larger grains containing low-angle grain boundaries (LAGBs; the misorientation between 2–15°) were found to exist (marked by arrows in Fig. 3a), i.e. shear reversed austenite displaying substructure. A very small fraction of unreversed martensite (red grains) was also detected. Similar features were present in the structure of the sample annealed at 800 °C within 10 s, though the large irregular-shaped grains with LAGBs were far more numerous and the amount of unreversed martensite also increased (Fig. 3b). After annealing at 800 °C for 10 s, few non-recrystallized DA grains were also observed, an example is given in Fig. 3c.
Fig. 2. Austenitic grain structure after annealing at 900 °C for 1 s. EBSD grain boundary map (a) and the orientation image map (b).

Fig. 3. Reversed grain structure after annealing at 850 °C-1 s (a) and 800 °C-10 s (b and c). Grains containing low angle grain boundaries pointed by arrows in (a), presence of irregular grain (b) and a non-recrystallized deformed austenite grain in (c). (Austenite gray, martensite red in color).
At lower annealing temperatures of 750–650 °C, the microstructures were strikingly different from those created at higher temperatures; some examples are shown in Figs. 4–7. The EBSD phase maps and Ferritscope measurements indicated clearly that even after a short annealing duration, the major phase was austenite with only a minor amount of unreversed martensite (red colored grains in phase maps), for instance 81% austenite after 1 s hold at 700 °C (not shown) and 86% after 10 s (Fig. 4a). The austenite consisted of refined grains, though with different sizes and various colors, as highlighted in the figures, but also green-colored, coarse elongated grains were present with the shape of the original cold-rolled grains, as can be seen in Figs. 4b, 5 and 6. They also contained a large number of LAGBs (white-colored boundaries). The fraction of fine grains became smaller in structures annealed at lower temperatures and correspondingly the fraction of large austenite grains with LAGBs increased (compare Figs. 4 and 7).

Fig. 4. Microstructure obtained after annealing at 700 °C for 10 s. Phase map (a) and OIM map (b). Martensite red-colored in (a).
Fig. 5. Microstructure obtained after annealing at 700 °C for 1800 s at two different magnifications (OIM maps).

Fig 6. Microstructure obtained after annealing at 650 °C for 3600 s. Martensite red in the phase map (left).
In addition to austenite, some retained DIM existed in the structures annealed at 800°C and lower temperatures (Figs. 4–7). The fraction after 1 s holding increased with decreasing annealing temperature from 8% at 800 °C to 12% at 750 °C and 19% at 700 °C. The unreversed DIM fractions after annealing at 750, 700 and 650 °C are plotted as a function of annealing time in Fig. 8. A complete list of DIM fractions at different annealing temperatures and /or times including the data plotted in Fig. 8 will be presented later in Table 3. It is seen that the DIM fraction decreased with prolonged soaking time, very fast at 750 °C and more slowly at 700 and 650 °C. Thus, the reversion phenomenon continued and was dependent on temperature and time.
Fig. 8. Fraction of martensite retained after annealing at 750, 700 and 650 °C for various annealing durations.

3.3. Grain size

As noticed from previous figures (Figs. 4–7), the GS after reversion treatment is not uniform and the non-homogeneity increases with decreasing the annealing temperature. To illustrate this, the area weighted GS distributions after various reversion conditions are plotted in Fig. 9, based on high angle grain boundaries (HAGBs; misorientation >15°) or both LAGBs and HAGBs (H&LAGBs) (Fig. 9 a and b, respectively). It is seen that after annealing at 800–900 °C, the peak in the area frequency is between 1–3 µm, though few much larger grains do also exist. GS distributions of structures obtained by reversion at 800-900 °C are more uniform (specially for HAGBs) compared to those at lower temperatures and the average GS is almost constant meaning that reversion is completed at these temperatures. A comparison of HAGBs and H&LAGBs also shows that the area fraction of LAGBs is quiet low for high temperatures indicating again the completion of reversion. The peak shifted to slightly smaller GSs while annealing was performed at 700 or 650 °C.
A distinct feature in the distributions is the appearance of large (30–50 µm) grains after annealing at low temperatures of 700 and 650 °C resulting from the existence of non-recrystallized DA grains. Another feature after the same conditions is a high fraction of LAGBs (Fig. 9b) highlighting the presence of subgrains in the shear reversed austenite and recovery in DA grains. The area fraction of LAGBs decreases with prolonged holding, especially at 700 °C as an obvious consequence of the progress of recovery and subgrain coalescence.

![Graph](image_url)

**Fig. 9.** Grain size distribution after reversion annealing at different conditions based on high angle grain boundaries (HAGBs) (a) or both HAGBs and low angle grain boundaries (LAGBs; misorientation 2–15°) (b).

### 3.4. Precipitation structure
Precipitation of Cu particles at surface region is required for the antibacterial property [1,4,6,9,12]. According to Luo et al. [12], the optimal aging is 1.5 h at 650 °C. Therefore, TEM, STEM and X-ray mapping were employed to check the presence of Cu after 1.5 h holding at 700 and 650 °C. Examples of the structure recorded on a sample annealed at 700 °C for 1.5 h are shown in Figs. 10–12. Also, an X-ray map revealing the distribution of Cu in the examined field is displayed in Figs. 10b and 11d. Selected area electron diffraction (SAED) patterns as presented in Fig. 10c–e were used to identify the austenite and martensite grains in the reversion treated microstructure. In Fig. 10a, a reversed austenite grain with low dislocation density (upper part), unreversed martensite and sheared austenite with subgrains are found to co-exist based on SAED patterns. The X-ray Cu map in Fig. 10b indicates that Cu precipitates did form and here they seem to be mainly distributed along specific zones (black channels) at phase, grain and subgrain boundaries. A local view of dislocation-free austenite grains is shown in Fig. 11, where Cu precipitates are distributed quite uniformly. White spots in bright field (BF) image in Fig. 11a are seen as black spots in dark field (DF) image in Fig. 11b, which appear as empty holes, where particles have fallen off during the foil preparation. White spots in Fig. 11c are particles rich in Cu, as also confirmed by X-ray map in Fig. 11d. The coherent character of the precipitates is shown in a TEM two-beam BF image in Fig. 12a. The coherence is further verified by high-resolution image of one particle (Fig. 12b).
Fig. 10. STEM micrograph after annealing at 700 °C for 1.5 h (a), the corresponding X-ray map (b) and electron diffraction patterns of austenite (c) and martensite (d and e) taken from areas marked in (a) by dashed circles.
Fig. 11. A local view of dislocation-free austenite grains in a sample annealed at 700 °C for 1.5 h. Bright field (a) and dark field (b) images revealing nano-size particles. A magnified view (c) of the square area marked with red line in (b) and corresponding X-ray map of Cu distribution in this area (d). Black spots in (c) are holes (i.e. lost precipitates) and are not seen in (d).
Fig. 12. A TEM 2-beam BF image revealing the coherence contrast of Cu precipitates in austenite (a) and an HR-STEM image of a Cu particle (b). Annealing at 700 °C for 1.5 h.

Figure 13 displays a local area in a sample annealed at 650 °C for 1.5 h, revealing dislocation-free austenite grains (or subgrains) which are surrounded by deformed structure. Coherent Cu precipitates could be detected in at least two grains, as pointed out. However, the presence or absence of precipitates in other grains has not been resolved. This would require further studies.
3.5. Tensile properties and strain-induced martensite

The objective of the applied reversion treatment applied was to improve the strength properties of the steel. The hot rolled sheet before the cold rolling had the YS of 286 MPa, UTS 553 MPa and TE 51%. The results from tensile tests of the reversion-treated samples are listed in Table 2 and corresponding engineering tensile stress-strain curves are plotted in Fig. 14. In reversion experiments, the lowest YS was 256 MPa after annealing at 950 °C for 100 s (microstructures or stress-strain curves are not shown here). It is seen that after 1h annealing at 700 °C, the YS value of the reversion-treated structure is about twice (≈524 MPa) higher than the lowest YS and jumps to a level about thrice (≈ 790–830 MPa) higher after annealing at 650°C. In Fig. 15, the influence of the annealing time at 750, 700 and 650 °C on the YS is shown, revealing fast drop of YS.
corresponding to annealing at 750 and 700 °C, but much less at 650 °C. The fracture elongation decreases slightly with increasing strength, but it stays around 36% even after annealing at 650 °C. Yielding however, appears to be the Lüders type after annealing at 650 °C for long times, although not so distinctly as obtained by Sun et al. [28], who reported a long Lüders strain of 10% for a reversion-treated structure of a 17Cr-6Ni-2Cu steel, annealed at 700 °C.

Table 2. Tensile properties of the 304Cu steel after various reversion annealing treatments compared to those of as-received (hot rolled) and cold-rolled conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)-Time (s)</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Uniform elongation (%)</th>
<th>Total elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>285</td>
<td>553</td>
<td>46.4</td>
<td>51</td>
</tr>
<tr>
<td>Cold-rolled</td>
<td>1228</td>
<td>1260</td>
<td>0.5</td>
<td>10.4</td>
</tr>
<tr>
<td>950-1</td>
<td>330</td>
<td>652</td>
<td>51.0</td>
<td>65.1</td>
</tr>
<tr>
<td>900-1</td>
<td>351</td>
<td>672</td>
<td>50.9</td>
<td>68.4</td>
</tr>
<tr>
<td>900-10</td>
<td>336</td>
<td>664</td>
<td>48.4</td>
<td>62.7</td>
</tr>
<tr>
<td>850-1</td>
<td>421</td>
<td>719</td>
<td>46.7</td>
<td>59.9</td>
</tr>
<tr>
<td>850-10</td>
<td>397</td>
<td>704</td>
<td>47.9</td>
<td>61.2</td>
</tr>
<tr>
<td>800-100</td>
<td>403</td>
<td>735</td>
<td>44.9</td>
<td>57.8</td>
</tr>
<tr>
<td>750-100</td>
<td>588</td>
<td>873</td>
<td>32.2</td>
<td>43.5</td>
</tr>
<tr>
<td>700-10</td>
<td>824</td>
<td>995</td>
<td>22.7</td>
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</tr>
<tr>
<td>700-100</td>
<td>776</td>
<td>972</td>
<td>23.9</td>
<td>35.1</td>
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<td>700-600</td>
<td>653</td>
<td>924</td>
<td>29.1</td>
<td>40.0</td>
</tr>
<tr>
<td>700-1800</td>
<td>602</td>
<td>898</td>
<td>29.2</td>
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<tr>
<td>700-3600</td>
<td>524</td>
<td>870</td>
<td>31.6</td>
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<td>700-5400</td>
<td>507</td>
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<td>650-3600</td>
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<td>791</td>
<td>1008</td>
<td>25.2</td>
<td>36.0</td>
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</table>
Fig. 14. Stress-strain curves of a cold rolled specimen and some reversion annealed ones in different conditions.

Fig. 15. Effect of annealing duration at 750, 700 and 650 °C on yield strength.
It is also seen that the stress-stress curves are convex in shape after annealing at temperatures of 800–900 °C, but they become concave soon after the start of yielding for samples annealed at 750–650 °C for 100 s or longer. The difference in tensile behavior becomes more evident in strain hardening rate (SHR) vs. true strain curves predicted from the stress-strain data, which are plotted in Fig. 16. The curves corresponding to reversion treatments at 750 °C and lower temperatures reveal peaks in the incremental strain hardening rate vs. true strain plots, whose height increases with prolonged duration at 700 and 650 °C. The maximum SHR of 3 GPa is obtained at 700 °C. The manifestation of a high peak suggests more significant α'-martensite formation during straining in the structures formed under certain conditions with close dependence on annealing temperature and holding time.
Fig. 16. Strain hardening rate as a function of true strain for the specimens annealed at different conditions: (a) 750–900 °C with varying holding times 10–100 s, (b) 700 °C/100–5400 s and (c) 650 °C/1800–5400 s.

DIM fractions in some samples, reversion annealed for short times, were measured before and after tensile testing and the values are listed in Table 3. In the table, the values of DIM formed during tensile testing are also given, based on the difference between the values after and before the tests. They indicate that the amount of DIM formed during straining to fracture does not depend on annealing duration and it only increases slightly with increasing the annealing temperature in the range of 850–950 °C, where minor change can be related to the coarsening of GS with increasing annealing temperature [26]. Instead, after annealing at 750 and 700 °C, the fraction increases with annealing time. This dependence is more readily seen in Fig. 17, where the amount
of new DIM formed during tensile straining to fracture is plotted as a function of annealing duration at temperatures of 750, 700 and 650 °C. The figure reveals that the amount of new DIM increases very significantly from about 50 to 90%, slightly faster corresponding to a higher annealing temperature. This means that the stability of austenite decreases as a consequence of annealing at these temperatures, and obviously due to the precipitation of Cu.

Table 3. Martensite content before and after tensile testing and formed during tensile test of samples annealed at different conditions.

<table>
<thead>
<tr>
<th>Temperature/Time</th>
<th>Before tensile testing</th>
<th>After tensile testing</th>
<th>During tensile testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 s</td>
<td>10 s</td>
<td>100 s</td>
</tr>
<tr>
<td>700 °C</td>
<td>18.9</td>
<td>14.0</td>
<td>10.8</td>
</tr>
<tr>
<td>750 °C</td>
<td>11.6</td>
<td>7.7</td>
<td>6.5</td>
</tr>
<tr>
<td>800 °C</td>
<td>7.8</td>
<td>6.6</td>
<td>2.8</td>
</tr>
<tr>
<td>850 °C</td>
<td>3.7</td>
<td>2.6</td>
<td>2.1</td>
</tr>
<tr>
<td>900 °C</td>
<td>2.8</td>
<td>2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>950 °C</td>
<td>2.8</td>
<td>2.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Fig. 17. The amount of new DIM formed during tensile straining of the samples annealed at 650, 700 and 750 °C for different durations.
3.6. Hardness

The hardness values of the reversion-treated samples after annealing at various temperatures for a short holding time of 1-100 s are plotted in Fig. 18. The corresponding hardness data following reversion annealing of 0.5 and 1 h durations for 304L steels, taken from Mészáros and Prohászka [29] and Martins et al. [30] respectively, are also included for comparison. The drop in hardness is steep in a temperature interval between 700–800 °C as shown by a green highlight in Fig. 18. In this temperature range, the amount of retained DIM decreases as seen in Table 3, but the softening continues at 850–950 °C, where no retained DIM existed. Excellent agreement can be noticed between the present and literature data also revealing an influence of prolonged annealing times on hardness, particularly at 700–800 °C.

Fig. 18. Hardness variation after annealing at different temperatures for 1, 10 and 100 s. Some data from Mészáros and Prohászka [29] for 1 h and Martins et al. [30] for 0.5 h are included.
4. Discussion

The results clearly indicated that the grain structure of the 304Cu steel could be modified by cold rolling and reversion annealing sequence resulting in an increase in the YS, while the elongation remained reasonably high. We discuss below the reversion process in general and the complex microstructures created in the temperature regime relevant to obtain the antibacterial property in this steel (≤ 750 °C) and assess the improvement of the strength achieved.

4.1. Reversion behavior

Different opinions have been presented so far on the characteristics of the reversion process in 304/304L steels with and without Cu alloying, so it is worthy to discuss shortly the mechanism and kinetics of the reversion. One practical variable in the reversion treatment is the thickness reduction in the cold rolling stage before the annealing. In relatively stable alloys such as the 304 grade, severe deformation is required at RT to obtain a structure consisting of 100% DIM; reductions of 90% or beyond being applied in some studies [14,31]. The Cu alloying further increases the stability of the steel by increasing its SFE and decreasing the $M_d$ temperature [10,11]. However, very high cold rolling reductions are not quite practical in industry. In this study, the steel was rolled to provide about 71% reduction, which resulted in the martensite fraction of about 80% (Fig. 1). This means that two deformed phases, DIM and DA, were present, which must be accounted for microstructure analysis. DA cannot, however, be refined to the same extent as the highly deformed DIM. Also, after gradual formation of DIM during cold rolling without a saturation stage, as is evident in the present case, a certain fraction of martensite remains as slightly deformed lath martensite and does not reverse in a manner similar to the highly deformed cell martensite [26,32–34]. The behavior of DA among DIM has been discussed in several papers, e.g.
Järvenpää et al. [26,34] have investigated in detail the evolution of grain structure after different cold rolling reductions (32–63%), i.e., containing various retained DA fractions in a 301LN steel, showing formation of complex structures after annealing, where GS can be classified in four classes, the fractions dependent on the annealing temperature, in particular.

The reversion mechanism in the 304 type stainless steel has been investigated in numerous studies, e.g. [18,28,35–39], but somewhat different opinions exist. Some researchers have reported that the diffusional reversion can occur at low annealing temperatures of 550–650 °C [36,39] and the shear reversion occurs at higher temperatures, e.g. above 750 °C [39]. The effect of heating rate has been observed, suggesting diffusional reversion at low heating rates (<10 °C/s) and shear reversion at higher ones (>40 °C/s) [28]. Consistently, Sun et al. [35] envisaged that fine austenite grains formed via diffusional reversion of martensite as using the heating rate of ≈ 10 °C/s. However, Cios et al. [37] and Ondobokova et al. [38] reported shear type reversion mechanism in the temperature range 400–700 °C and 600–800 °C, respectively. Even the concurrent operation of both the diffusion and shear mechanisms have also been claimed [18].

Tomimura et al. [40] have shown that an increase in the Ni/Cr ratio causes an increase in the Gibbs free energy change between the fcc and bcc structures and thereby lowers the martensitic shear reversion temperature. The ratio Cr/Ni ≈ 0.63 was found to favor the shear reversion mechanism in their experiments. In the present steel, Ni/Cr is low, about 0.42, so the diffusional reversion would be preferred. However, in addition to Ni, Cu too is an austenite stabilizing element (with the same power as Ni in \( M_d \) [25]), and therefore we can expect it to favor the shear reversion mechanism, but even the \((\text{Ni}+\text{Cu})/\text{Cr} ≈ 0.54\) is not very high in the present instance. However, a
high heating rate of 200 °C/s was used in the annealing experiments, so this may be the main reason for the occurrence of the shear mechanism, in agreement with the observations of Sun et al. [28]. A firm evidence for the shear reversion, as seen in Fig. 19, is that the structure is almost fully coarse-grained austenite even after very short annealing time of 10 s at 700 °C (a decrease of the DIM fraction from 80% to 19%, Table 3, also seen in Fig. 4). This implicates that the reversion has been very fast, i.e., faster than those employed in the experiments of Sun et al. [28], who found that only 25% of DIM reversed within 2 min at 700 °C. The shear mechanism is evident also from the elongated shape of austenite grains after annealing at 650 and 700 °C (Figs. 4-7), containing traces of prior α’-martensite morphology, as a clarifying feature of the shear reversion [40]. After this fast reversion transformation, subgrains are formed in reversed austenite which coalesce into a structure resembling the defect-free recrystallized structure with time. The occurrence of continuous recrystallization mechanism is demonstrated in local views in Fig. 19, depicting two examples.

Fig. 19. Formation of defect-free austenite grains during annealing at 700 °C for 10 s (a) and 600 s (b) indicating the shear reversion mechanism followed by continuous recrystallization. Low angle grain boundaries are white lines in the orientation image map (a), and martensite is red in the phase map (b).
After low-temperature annealing, very pronounced size differences appear in dislocation-free grains (concluded from a high image quality (IQ) in EBSD images), as shown in Fig. 20. There are fine grains but also large grains (few microns), often in groups, and one might speculate that the large grains have formed by the local occurrence of diffusional reversion. A low temperature of 650–700 °C would favor diffusional reversion in 304 type steel [36,39]. Takaki et al. [32] demonstrated that in the diffusional reversion from lath-type martensite, i.e. from slightly deformed martensite, austenite nucleates on lath boundaries with a shape of thin plate and that the same kind of austenite gathers in a group forming blocks with certain orientation. One kind of austenite grains nucleate within one martensite block and the reversed austenite inherits the morphological characteristics of lath-martensite even in a diffusional reversion. However, in the present instance, these grains do not have a lath shape, but they are largely equiaxed or have a typical subgrain shape, though large in size. These grains are surrounded by areas of subgrains, where new strain-free grains are forming by continuous recrystallization, obviously as a follow-up of the shear reversion. Therefore, it seems that even these large dislocation-free grains are formed very quickly from the shear reversed austenite, which in turn has formed from slightly deformed martensite. Some of these grains still contain LAGBs inside (see Fig. 20a).
Fig. 20. Examples of big difference in the grain size in reversed dislocation-free grains after annealing at 700 °C for 10 s (a,b) and 600 s (c,d). DA is retained deformed austenite grain (a). Martensite is in red in the phase map (b,d).

The DA grains are always green in color, i.e. Brass oriented, as in Fig. 20a (a DA grain marked), showing the highest stability [26,41]. They can be distinguished from reversed coarse grains on the basis that hardly any new grains would have formed in them after short time annealing (DA in Fig. 20a) and often long parallel shear bands are also seen in them (see Figs. 4 and 6). Recrystallization of DA is a slow process, starting in 1 h at 700 °C [30,42]. Larger grains seen after annealing at 850–900 °C are formed from the DA by recrystallization (Figs. 2 and 3), which
can also be concluded from the GS distribution in Fig. 9. However, it has been found that the continuous recrystallization by formation of subgrains and their evolution to grains can also happen in DA grains [26].

A special feature in the present microstructures is that some α′-martensite exists even after annealing for 1.5 h at 650–700 °C. However, it is clearly seen that the DIM content decreased during isothermal holding at temperatures below 850 °C (Fig. 8, Table 3). This can be explained by the occurrence of diffusional reversion following shear reversion. Tomimura et al. [40] have presented the time-temperature-reversion (TTR) diagram to describe the reversion under different heating-annealing conditions. In Fig. 21, the reversion start and finish temperatures are shown for the shear and diffusional reversion mechanisms (A_s', A_f' and A_s, A_f respectively). Thus, under certain conditions: at a high heating rate to the regime between A_s' and A_f' results in partial reversion by the shear mechanism. In the two-phase regime, during isothermal holding, the diffusional reversion starts at time corresponding to A_s and becomes completed at time corresponding to A_f. Shakhova et al. [18] predicted and observed A_f around 800 °C for S304H. Also for the present steel, A_f' can be evaluated as or slightly above 800 °C from the data in Table 3. Martins et al. [30] and Shakhova et al. [18] reported reversion starting between 500–550 °C for a 304L and S304H steels, respectively, and Shakhova et al. [18] measured about 8% and 20% DIM (ferrite) at 700 and 650 °C for 30 min, respectively. In the present experiments, some DIM (ferrite) still remains in the structure at 700 and 650 °C, although the decrease seems to continue at 700 °C after 1.5 h. Based on this information, the approximate scales are drawn in the TTR diagram in Fig. 21 and a processing route at 700 °C for 5400 s is shown comprising two successive reversion mechanisms leading to partial reversion.
Luo et al. [12] mentioned that martensite is formed during an annealing treatment for the antibacterial property. Of course, martensite cannot form at such a high temperature, but a bcc phase is retained during annealing below a certain temperature. Also in the experiments of Cios et al. [37], Shen et al. [43], Mészáros and Prohászka [29], Odnobokova et al. [38], and Shakhova et al. [18], up to 10% martensite was left unreversed at 700 °C (after 0.5–1 h), in agreement with the present observation (Figs. 6 and 7).

According to Luo et al. [12], the presence of a small amount of martensite has no effect on the precipitation of the Cu-rich phase, so it does not affect the antibacterial properties of the sample. However, we may need to address a concern of the pitting corrosion resistance of the structure,
which may be detrimentally affected by the presence of the martensite phase \[44\], further debilitated by the Cu precipitation \[3,4,9,45\]. This needs further studies.

4.2. Precipitation kinetics

It is known that in supersaturated ferrite, Cu-rich coherent clusters, initially also rich in Fe, nucleate fast. During growth, these bcc-Cu pre-precipitates run through two structural transformations, viz. twinned 9R and untwinned 3R, until they ultimately transform to the equilibrium fcc structure of pure Cu with an incoherent interphase boundary \[46–48\]. Segregation of Cu on grain boundaries is accompanied with the cluster formation, too. However, in austenite, the precipitation of Cu-rich phase is just a gradual chemical composition change without any transformation of crystallographic structure, because both the Cu-rich phase and austenitic matrix have the same fcc crystallographic structure and close lattice parameters.

As regards the duration of aging needed for the precipitation, Hong and Koo \[4\] showed that an ageing time of 4 h at 700 ºC is long enough for a 304-2.5Cu steel to generate sufficient Cu-precipitates for the antibacterial property. Chi et al. \[49\] detected Cu segregated areas after 1 h aging at 650 ºC in a 304-Nb-N-3Cu alloy which developed into coherent particles keeping a fine size of 34 nm even until 10000 h. Also, Luo et al. \[12\] observed Cu-rich precipitates of 15 nm in size in a 304L-3Cu alloy after 1 h annealing at 650 ºC and found that the optimal heat treatment process comprised aging at 650ºC for 1.5 h, following solid solution at 1050 ºC for about 30 min. Recently, Luo et al. \[24\] reported the existence of coherent Cu particles and good antibacterial property in a 304L-3Cu alloy after aging for 30 min at 750 ºC.
All the same, the above aging experiments have been performed for annealed austenite. In the present instance, the initial structure is mainly deformed DIM (about 80%), from which the austenite is shear reversed that contain a higher density of dislocations and subboundaries, which later annihilate or coalesce to form dislocation-free austenite grains. In addition to shear reversed austenite, there is about 20% DA, containing recovered structure, and a small fraction of retained DIM. The precipitation kinetics can be much faster in martensite and dislocated austenite compared to that in the annealed austenite. Stechauser and Kozeschnik [47] have presented a TTP-diagram based on simulation and also experimental data for the Cu precipitation in bcc α-iron, and accordingly, the precipitation would start in 100 s at 600–700 °C and be completed within an hour. Soylo and Honeycombe [50] found coherent Cu-rich bcc zones in martensite/ferrite in a 30Cr-8Ni-3Cu steel quenched from 1300 °C, followed by reversion annealing at 700 °C for 30 s, and within 1 min incoherent fcc particles developed from them. During the reversion annealing of cold rolled 301LN steel, precipitation of CrN has been found to occur within few seconds at 700 °C [51,52]. Thus, the precipitation can be very fast, if it occurs in bcc structure and a high dislocation density further accelerates it [7].

On the other hand, it is noteworthy that the shear reversion was very fast, so that the reversion was almost completed on heating at 200 °C/s and holding for 1 s at 700 °C, for instance. Therefore, this duration does not provide much time for the Cu precipitation in the DIM. The coherence of the particles in the austenite grain (as seen in Figs. 12 and 13) means that they have the fcc structure, but it is difficult to know if they formed in DIM or austenite. Hence, we have to conclude that the present circumstances for the precipitation are complex and this study cannot reveal and explain them, but only demonstrates that the Cu precipitation has occurred during the reversion treatment.
at 650–700 °C for 1.5 h, as is evident from Figs. 10–13. A shorter time might be enough for the purpose, even beneficial for the strength, but this needs to be ascertained in a future study.

Tensile stress-strain and SHR curves (Figs. 14 and 16, respectively) might also augment further information regarding the precipitation kinetics. The evolution of the YS does not give such information, as it is affected by changes in dislocation structure in austenite and also the decrease of the retained DIM fraction. However, a pronounced change in the stability of austenite occurred, appearing as a peak in SHR curves (Fig. 16), after annealing at 750–650 °C, being dependent on aging time. Also, the martensite fraction formed during tensile straining increased (Table 3; Fig. 17). The dependence of the stability on the previous annealing treatment can be connected with the precipitation of Cu out of the solid solution, while the austenite stability decreases. From Fig. 16, it can be seen that at 700 °C, an annealing duration of 600 s resulted in the maximum SHR of 2 GPa, though even 100 s annealing at 750 °C caused a similar peak of 2 GPa, but at 650 °C about 1 h was required to reach that peak level. Thus, at 700–750 °C, time even shorter than 0.5 h seems to be adequate to result in pronounced precipitation of Cu, but the process continues at least until 1.5 h, as is evident from Figs. 16 and 17.

4.3. Enhanced strength

As regards the targeted strength, the results of the reversion annealing experiments carried out for a 304L-3.15Cu steel indicate that the YS can be improved significantly without impairing its ductility considerably. Hence, excellent YS-TE combinations are possible to achieve, similarly as reported in numerous studies for various austenitic stainless steels earlier. In Fig. 22, some YS-TE combinations, taken from Table 2, are included in the data shown in Ref. [15] for reversion treated
Cr-Ni steels. It can be realized that the present results are quite typical for reversion treated structures, although at a lower regime. Thus, from the figure it is possible to estimate and conclude which mechanical properties can be achieved for 304Cu steel, if other properties are not taken into account.

Fig. 22. Yield strength versus total elongation after different reversion conditions compared to reversion treated 3XX grade austenitic stainless grades (data from Ref. [15])

Järvenpää et al. [15] have recently presented an overview of the Hall-Petch type relationships presented for reversion-treated austenitic stainless steels and pointed out a broad scatter between proposed relationships. Shakhova et al. [18] suggested a relationship between the YS (in MPa) and GS (D in µm) for grain-refined Cr-Ni/Cr-Ni-Cu steels (Eq. 2):

\[
YS = 205 + 395 \ D^{0.5} \tag{2}
\]
To check briefly the relevance of that equation, the number weighted average GS and corresponding calculated and measured YS for different reversion conditions are listed in Table 4. For structures created at high annealing temperatures (at 800 °C and above), obviously the GS has an important contribution, although it seems that the present YS values are relatively low compared to those reported for 304 [13], 301LN [15,33,34] and 204Cu [19] steel at a given GS. After annealing at lower temperatures, in addition to GS, the retained phases and dislocations contribute to the YS in addition to grain boundaries so that any simple relationship cannot be expected. From the present results, it is seen that the measured YS is distinctly higher than the predicted one.

Table 4. Number weighted average GS and corresponding calculated and measured YS after reversion annealing at different conditions (°C-s).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>650-3600</th>
<th>650-5400</th>
<th>700-10</th>
<th>700-600</th>
<th>700-1800</th>
<th>700-3600</th>
<th>800-10</th>
<th>850-1</th>
<th>900-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGS (Intercept)</td>
<td>0.6</td>
<td>0.9</td>
<td>0.6</td>
<td>0.9</td>
<td>0.7</td>
<td>0.9</td>
<td>1.3</td>
<td>1.24</td>
<td>1.72</td>
</tr>
<tr>
<td>Calculated YS</td>
<td>715</td>
<td>621</td>
<td>715</td>
<td>617</td>
<td>677</td>
<td>621</td>
<td>551</td>
<td>560</td>
<td>506</td>
</tr>
<tr>
<td>Measured YS</td>
<td>812</td>
<td>791</td>
<td>824</td>
<td>653</td>
<td>602</td>
<td>524</td>
<td>416</td>
<td>421</td>
<td>351</td>
</tr>
</tbody>
</table>

It can be pointed out that the GS obtained at low reversion annealing temperatures is neither very fine, nor uniform. However, recent studies have indicated that complex structures with non-uniform GS and non-recrystallized retained austenite among the reversed fine grains can provide good mechanical properties [36,53–55]. Bimodal GS has been shown to enhance ductility [55]. Anyhow, it is important to note that an enhanced strength, for instance, YS to the tune of 812 or 791 MPa can be achieved on reversion annealing at 650 °C for 1 and 1.5 h respectively, i.e. under the conditions where the Cu precipitation has been found to be sufficient for the antibacterial property even in annealed austenite [12]. At 700 °C, with the same aging treatment, the YS of about 507–524 MPa can be achieved, which is still almost double compared to that of the annealed state.
According to a review of Bauer et al. [56], the 316L grade itself can be used as 30% cold rolled, while its YS is around 790 MPa. However, cold rolling then must be carried out as a separate operation after the precipitation aging, if the antibacterial property is desired.

Finally, we again highlight that in addition to improved static and fatigue strength, ultrafine grain-refined austenitic stainless steels have greater open lattice in the position of high angle grain boundaries and high hydrophilicity [22,23,57–59]. Therefore, they have been found to possess favorable enhancement of osteoblast functions, protein adsorption on surface and consequently improved cell attachment, proliferation, and expression level of actin, vinculin and fibronectin. This may be a factor to favor the adoption of grain-refined austenitic stainless steel as an implant material.

5. Summary

Various reversion treatments were applied to a 304L-3.15Cu austenitic stainless steel with the objective to improve significantly its yield strength without considerably impairing ductility, under conditions suitable for the antibacterial property. Microstructures were characterized and hardness and tensile properties determined. The main observations and conclusions are as follows:

The 71% cold rolling reduction results in the structure containing about 80% deformation-induced martensite and 20% retained deformed austenite.
Short reversion annealing (1–100 s holding) at 800–900 °C results in fully austenitic grain structure with the average grain size of few microns, but also larger grains inherited from retained austenite grains exist.

At lower annealing temperatures of 700–650 °C, the reversion occurred very fast by the shear mechanism, further followed by the diffusional mechanism. Depending on the annealing duration (1 s up to 1.5 h), the complex structure consisted of reversed grains with different sizes (below one micron and few microns), large grains with subgrains (which coalesce and recrystallize with the continuous recrystallization mechanism), large retained austenite grains and a small amount of retained martensite (ferrite).

Cu-precipitation occurred during annealing at temperatures of 750–650 °C, concluded from the decrease in the stability of austenite and increase of strain hardening rate in tensile tests and the observations made by transmission electron microscopy.

This study reveals that following the grain size refinement and retained phases obtained by the reversion annealing treatment at 700–650 °C for 1–1.5 h, the yield strength of the present 304L-3.15Cu steel increases by 2–3 times that of the annealed structure, while the ductility remains high. Based on the occurrence of Cu-precipitation, it can be concluded that the antibacterial property is obtained under these conditions.

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