Reverse-transformation austenite structure control with micro/nanometer size

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Abstract: To control the reverse-transformation austenite structure through manipulation of the micro/nanometer grain structure, the influences of cold deformation and annealing parameters on the microstructure evolution and mechanical properties of 316L austenitic stainless steel were investigated. The samples were first cold-rolled, and then samples deformed to different extents were annealed at different temperatures. The microstructure evolutions were analyzed by optical microscopy, scanning electron microscopy (SEM), magnetic measurements, and X-ray diffraction (XRD); the mechanical properties are also determined by tensile tests. The results showed that the fraction of strain-induced martensite was approximately 72% in the 90% cold-rolled steel. The micro/nanometric microstructure was obtained after reversion annealing at 820–870°C for 60 s. Nearly 100% reversed austenite was obtained in samples annealed at 850°C, where grains with a diameter ≤ 500 nm accounted for 30% and those with a diameter > 0.5 μm accounted for 70%. The micro/nanometer-grain steel exhibited not only a high strength level (approximately 959 MPa) but also a desirable elongation of approximately 45%.

Keywords: austenitic stainless steel; structure control; martensite; reverse transformation; grain refinement

1. Introduction

Austenitic stainless steels have been widely used in artificial joints and other biomedical materials because of they are non-magnetic, corrosion-resistant, easy to shape, and exhibit good mechanical properties [1]. Their only drawback is that the biocompatibility of austenitic steel is obviously inferior to that calcium phosphate and bioactive glass. Misra *et al.* [2–5] have authored several recent reviews related to the biomedical applications of ultrafine-grained steel. They noted that nanocrystals with sizes of 500 nm or less tend to improve cell viability and promote the formation of bone lipoprotein. Micron-sized grains (0.5–2 μm) can facilitate cell adhesion and stimulate metabolic activity, which imparts austenitic stainless steels with a micro/nanometer composite structure with better human histocompatibility compared to that of the traditional coarse-grained medical stainless steel.

Microstructure is one of the most important factors determining the mechanical properties of steel materials. Many microstructure control technologies have emerged in the

course of development of the traditional structural steels to improve their mechanical performance [6–11]. Steel materials with excellent combinations of strength and toughness have been obtained through various microstructure refinement technologies. From the late 1990s to the beginning of this century, research on the ferrite refinement limit was carried out in Japan, South Korea, the European Union, and Australia, among other countries. In the same period, the theory of deformation-induced ferrite phase transition (DIFT) was proposed by researchers in China [12–13]. Their results demonstrated that the yield strength of carbon structural steel was improved from 200 to 400 MPa when the ferrite grains were refined from 20 to 5 μm . The yield strength of the micro-alloyed steel was improved from 400 to 700 MPa when the grain size was refined from more than 10 μm to 2 μm . The strength of the bainite/martensite multiphase microstructure was also significantly improved by refinement. It was based on the bainite transformation theory proposed by Bhadeshia's group [14] at the University of Cambridge, who designed a high-carbon steel with a bainite transformation temperature under 200°C. The bainite laths size was re-

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finned to the nanometer level, and the residual austenite with high toughness was retained in the microstructure, which resulted in a hardness of 600 HV and a strength of 2500 MPa. However, many approaches to refining grains are not suitable for stainless steel. For instance, the thermomechanical control process (TMCP) generally results in a coarse grain size on the order of 20 to 40 μm depending on the processing conditions.

We hypothesized that, if the microstructure of 316L stainless steel could be processed into a micro/nanometer composite microstructure, it would not only exhibit good biocompatibility, but also a good combination of strength and plasticity. Therefore, in this work, we investigated how to achieve grains with a micro/nanocomposite structure in 316L steel using special microstructure control technology.

2. Experimental procedure

The chemical composition of the 316L austenitic stainless steel was (in wt%) C 0.025, Si 0.66, Mn 0.79, Cr 16.8, Ni 10.2, Mo 2.16, N 0.09, and balance Fe. The tested steel sheet was obtained by the hot rolling process. The samples were heated to 1050°C and maintained at this temperature for 12 min for solution treatment. The initial austenite grain size was in the range from 5 to 20 μm , as shown as in Fig. 1. Cold deformation with 40%, 60%, 80%, and 90% total thickness reduction was carried out in this work. The annealing experiments were carried out on a CCT-AV-II annealing simulation machine for the samples with the different cold deformation reductions. The heating rate was 30°C/s to a holding temperature ranging from 700 to 1000°C; the soaking time was 60 s on continuous annealing.

The microstructural evolutions were analyzed using optical microscopy (Zeiss Axiovert 40MAT) and scanning electron microscopy (ZEISS ULTRA 55). A Feritescope (Quantum Design-PPMS) was used to measure the amount of ferromagnetic martensite phase. X-ray diffraction (XRD) measurements (Rigaku DMAX-RB with Cu K_α radiation) were used to identify the phases. All specimens were prepared by electropolishing at a voltage of 15 V for 25 s, where the electrolyte was composed of 20 vol% perchloric acid and 80% ethanol [15]. Electron backscatter diffraction was used for microscopic characterization. *In situ* tensile tests were carried out on the *in situ* tensile experiment table of the JEM-2100 transmission electron microscope. The tensile tests were carried out at room temperature using a CMT5105 tensile machine. Vickers microhardness values were measured on a HV-1000 micro-Vickers durometer.

Fig. 1. Original grain structure of the as-received coarse-grained sheet.

3. Results and discussion

3.1. Effect of cold deformation on strain-induced martensite transformation

The XRD results before and after cold deformation of 316L austenitic stainless steel are presented in Fig. 2. Only three diffraction peaks were observed for the samples without cold deformation; these peaks correspond to the (200), (220), and (311) crystal planes, respectively. That is, the microstructure of the solution-treated samples exhibited fully austenitic structures. Two new peaks attributable to body centered cubic (bcc) martensite appeared after cold deformation. The diffraction planes corresponding to these two peaks were the bcc (200) and (211) planes. The austenitic diffraction peak intensity gradually decreased and the martensite diffraction peak intensity gradually increased with increasing extent of cold deformation, as shown as in Fig. 2. The volume fraction of the strain-induced martensite in the 90% cold-rolled samples was approximately 72%, as shown in Fig. 3.

Fig. 2. X-ray diffraction patterns of the cold-rolled 316L stainless steel.

Fig. 3. Volume fraction of martensite and hardness of 316L stainless steel subjected to different cold-rolling reductions.

The original sample was almost non-magnetic, and the austenite fraction was nearly 100%, as shown in Fig. 4. The saturation magnetization (M_s) gradually increased with increasing cold deformation, which indicates that the volume fraction of martensite increased with increasing cold deformation.

According to the peak positions shown in Fig. 2 as well as the samples' magnetic characteristics after cold deformation, we concluded that the austenitic phase transformation occurred in the 316L stainless steel and that the new peaks

after cold deformation were the diffraction peaks of bcc-structured martensite. The strain-induced martensite fraction increased with increasing cold deformation. The twins, the grain deformation degree, and the crystal defects also increased with increasing cold deformation [16]. The elongated grains along the rolling direction exhibited flat or striped shapes. Greater cold deformation resulted in greater grain elongation. The grain boundaries became blurred, and the individual grains were indiscernible, exhibiting a fibrous structure when the cold deformation reached a certain extent, as shown as in Fig. 5.

Fig. 4. Magnetic hysteresis loop of 316L stainless steel samples subjected to different cold-rolling reductions.

Fig. 5. SEM micrographs of the grain structure of 40% (a) and 90% (b) cold-rolled sheets.

3.2. Reverse transformation of austenite after annealing

The microstructures were determined by the reverse-transformation kinetics, which, in turn, was related to the cold deformation [17–18]. The metastable austenitic phase was transformed to the martensite after cold deformation, and the strain-induced martensite lath structure was destroyed preferentially via the large deformation to the refined structure during the cold rolling [16]. Many boundaries were present in the fine grain structure, which provided advantageous sites for recrystallization nucleation; thus, the grain structure favored grain refining of the reversed

austenitic transformation by the large deformation [19]. The annealing experiments were carried out for samples subjected to 90% cold deformation. Fig. 6 shows the XRD results. The fraction of reversed austenite increased with the increasing annealing temperature. The austenite volume fraction was approximately 63% in the sample annealed at 750°C for 60 s, but increased to 74% when the annealing temperature was increased to 800°C for 60 s. The austenite percentage was approximately 94% in the sample annealed at 820°C for 60 s, and the specimen annealed at 850°C for 60 s was completely reversed to austenite (nearly 100%).

Fig. 6. X-ray diffraction patterns of 90% cold-rolled sheet specimens subjected to reversion annealing at different temperatures.

The microstructures of the samples with 90% cold deformation and annealed at different temperatures are shown in Fig. 7. The large deformation of the samples provided a high nucleation rate that resulted in more austenite grains in the subsequent annealing process. The distribution of austenite grain size in the sample annealed at the different temperatures is shown in Table 1. The austenite fraction with a grain diameter ≤ 500 nm accounted for 38%, and the austenite fraction with a grain diameter > 0.5 μm accounted for 62% for the samples annealed at 800°C for 60 s. The austenite fraction with the grain diameter ≤ 500 nm accounted for 35%, and the austenite with the grain diameter > 0.5 μm accounted for 65% for the samples annealed at 820°C for 60 s.

The microstructures were substantially refined compared to the original sample austenite grains, and Fig. 7 shows the reversed austenite with the micro/nanometer composite structure. The coarse austenite did not transform into martensite during the cold deformation process. The microstructure transformation was mainly related to the evolution of the new fine austenite during the annealing process, and the fine and equiaxed grains were transformed from the fragmentized martensite laths formed via the cold deformation process. That is, the formation of new fine austenite grains was a result of the reverse transformation. Although the grains with a diameter ≤ 500 nm accounted for 30% of the total grains, and the grains with a diameter > 0.5 μm accounted for 70% of the total grains in the samples annealed at 850°C for 60 s, grain growth was not obvious compared to the samples annealed at 820°C. Furthermore, the strain-induced martensite was completely reversed to austenite (close to 100%) when the samples were annealed at 850°C. The grains larger than 0.5 μm accounted for 73%, and the

Table 1. Effect of annealing temperature on the grain size (60 s)

Temperature / °C	$d \leq 0.5 \mu\text{m}$	$0.5 \mu\text{m} < d \leq 1.0 \mu\text{m}$	$d > 1.0 \mu\text{m}$
800	38%	36%	26%
820	35%	5%	30%
850	29%	31%	40%
870	27%	31%	42%
900	23%	25%	52%
950	17%	16%	67%

Fig. 7. Grain structures of the 90% cold-rolled sheet after reversion annealing at different temperatures for 60 s: (a) 820°C; (b) 850°C; (c) 870°C; (d) 950°C.

grains with a diameter ≤ 500 nm accounted for 27% in the samples annealed at 870°C for 60 s, as shown as in Fig. 7(c). In addition, the grains were not obviously coarsened compared to those of the samples annealed at 850°C. When the annealing temperature was 900°C, the grains began to grow and the grains with a diameter ≥ 500 nm accounted for 78%. We concluded that the microstructure with a small size grain was obtained by the shear reverse transformation in a very narrow temperature range [20]. The diffusion reverse transformation occurred with increasing temperature, which led to grain coarsening. The grains with a diameter > 0.5 μm accounted for 83% in the samples annealed at 950°C, and the grains obviously grew, as shown in Fig. 7(d). Therefore, when the strain-induced martensite is transformed into austenite, the annealing temperature should be as low as possible to control the grain growth [21]. On the basis of the aforementioned analysis, the micro/nanometer composite structure was obtained when the samples were annealed at 820–870°C for 60 s, and the scheme with an annealing temperature of 850°C for 60 s was optimal.

3.3. Mechanical properties

The mechanical properties of the samples with 90%

deformation and annealed at different temperatures are shown in Fig. 8. With increasing annealing temperature, the hardness decreased gradually. The changes in hardness were likely related to the defect density, the amount of strain-induced martensite, and the grain size of the reverse-transformation austenite. The hardness of the samples with 90% deformation was 476 HV₅₀. As shown in Fig. 8, the decrease of hardness was slow for samples annealed below 800°C. However, when the annealing temperature exceeded 800°C, the hardness decreased dramatically. The hardness decreased from 349 HV₅₀ for the sample annealed at 800°C to 256 HV₅₀ for the sample annealed at 820°C. In addition, in the sample annealed in 820°C, the strain-induced martensite had largely disappeared. When the annealing temperature was in the range from 820 to 870°C, the changes in hardness were not obvious because the microstructure of the samples did not obviously change and almost fully recrystallized in this temperature range. Furthermore, grain growth was also not obvious. Subsequently, the hardness was further decreased with increasing annealing temperature because of the substantial growth of austenite grains and the decrease of the dislocation density.

Fig. 8. Mechanical properties of the 90% cold-rolled sheet after reversion annealing at different temperatures.

As the annealing temperature increased, the tensile strength decreased; however, the elongation was gradually enhanced. The elongation was small when the samples were annealed at 750°C or 800°C, where the effects of work hardening were still observed. The microstructure did not obviously change compared to that of the cold-deformed specimens. A large amount of twins, dislocations and martensite were still present, which made the mechanical properties change only slightly. The elongation increased sharply when the samples were annealed at 820°C, and the mechanical properties were improved substantially. The product of strength and elongation increased from 16340 MPa·% to 41001 MPa·% when the annealing temperature was increased from 800°C to 820°C at an annealing time of 60 s.

This increase is attributed to microstructure defects being further eliminated with increasing annealing temperature. Meanwhile, the recrystallized grain size of the specimen annealed at 820°C was very small, which contributes greatly to the strength. Therefore, the elongation increased while the samples retained a high tensile strength. The mechanical properties were further improved when the annealing temperature was increased to 850°C, and the product of strength and elongation reached 42782 MPa·%. Furthermore, the strain-induced martensite had been completely reversed to austenite. The grain size changed little compared to that of the specimen annealed at 820°C; therefore, strength and plasticity matched much better than those of the original 316L austenitic stainless steel sample. The tensile strength reached

959 MPa, and the elongation was 45%; by contrast, the tensile strength and elongation of the original specimen were only 664 MPa and 58%, respectively, and the austenite grain size of the original samples was in the range from 5 to 20 μm .

In the case of the sample subjected to 90% cold deformation and annealed at 850°C for 60 s, the grains with a diameter ≤ 500 nm accounted for 30% and those > 1.0 μm accounted for 39%. Therefore, a composite structure of micro/nanometer grains was obtained. The grains were not obviously coarsened when the samples were annealed at 870°C for 60 s, and the elongation increased while the tensile strength was not substantially diminished. However, secondary recrystallization occurred when the annealing temperature was increased further, as shown in Fig. 7(d); in addition, some grains with abnormal growth were found, and these grains led to dramatically decreased tensile strength. In the case of samples annealed at 950°C for 60 s, the product of strength and elongation was reduced to 36422 MPa·%, which is even lower than that of the original sample (38203 MPa·%). Compared with the microstructure of the original sample, the grains obviously grew. Meanwhile, the micro/nanocomposite structure of the grains gradually disappeared when the samples were annealed at 950°C. A small amount of carbides precipitated along the grain boundaries, which led to the decrease of the mechanical properties.

3.4. Coordinating role of micro/nanograins in the deformation process

To elucidate the mechanism of the coordinated deformation

for micro/nanocomposite-structured grains, we carried out *in situ* tensile tests. The movements of dislocations in the micro/nanocomposite-structured grains during the deformation are shown in Fig. 9. The dislocations originated in the large grains (micrograins), and its movement was hindered by grain boundaries. In addition, smaller grain sizes resulted in a larger grain-boundary area. Therefore, the movement of dislocations in the fine grains became increasingly difficult. Of course, the slip band can also move transversely. In addition, with constant movement of the slip bands, dislocation pile-up occurred in the boundaries, as shown in Fig. 9(b). However, the slip bands continued to move when the dislocation pile-up reached a certain extent. The dislocation pile-up occurred in the nanograin boundaries, and the multi-directional movement of slip bands can avoid stress concentration. The further expansion of cracks in the smaller grains can be prevented through releasing the stress of the twin. The large grains easily deformed, whereas the small grains were relatively stable. The dislocations moved along the nanoscale grain boundaries and formed a dislocation cell because of the blocking of grain boundaries when the dislocations moved to smaller grains, as shown in Fig. 9(c). The large grains (micrograins) first deformed, which contributed to the plasticity. When the deformation of large grains reached a certain extent, the small grains (nanograins) began to deform, which contributed to the strength. Moreover, the large grains and small grains were well matched in the samples annealed at 850°C for 60 s, where the product of strength and elongation reached its highest value among the investigated samples.

Fig. 9. Movements of dislocations in the micro/nanostructure: (a) micro/nanostructure; (b) dislocation pile-up; (c) dislocation cell.

4. Conclusions

(1) The diffraction peak intensity of martensite and the M_s increased with increasing cold deformation of 316L stainless steel. When the cold deformation was 90%, the strain-induced martensite fraction was approximately 72%. The grains were elongated along the direction of deformation. Large amounts of deformation twins, lath martensite, and high-density dislocations were present.

(2) After 90% cold rolling, the micro/nanocomposite structure was obtained when the samples were annealed in the range from 820 to 870°C for 60 s. The fraction of austenite approached 100% when the samples were annealed at 850°C for 60 s, whereas grains with a diameter ≤ 500 nm accounted for 30% and grains with a diameter > 0.5 μm accounted for 70%. The steel with the micro/nanocomposite structure not only exhibited a high strength level (approximately 959 MPa) but also exhibited a desirable elongation (approximately 45%), which resulted in a better match of the strength and plasticity compared to the case of the original 316L stainless steel.

(3) The large grains (micrograins) were more easily deformed, which contributed to the plasticity. When the deformation of large grains reached a certain extent, the small grains (nanograins) started to deform. Therefore, the main contributor to the strength was the small grains.

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