Journal of Ultrafine Grained and Nanostructured Materials
Vol.48, No.1, June 2015, pp.53-58

Martensite phase reversion-induced nano/ ultrafine grained AISI 304L stainless steel with magnificent mechanical properties

Mohammad Shirdel[1], Saber Neisi-Minaei[1], Hamed Mirzadeh[1*] , Mohammad Habibi-Parsa[1,2,3]

1. *School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran*
2. *Center of Excellence for High Performance Materials, School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran*
3. *Advanced Metalforming and Thermomechanical Processing Laboratory, School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran*

Received: 19 November 2015; Accepted: 15 April 2015
* *Corresponding author E-mail: hmirzadeh@ut.ac.ir, Tel.: +98 21 82084127; Fax: +98 21 88006076*

Abstract
Austenitic stainless steels are extensively used in various applications requiring good corrosion resistance and formability. In the current study, the formation of nano/ ultrafine grained austenitic microstructure in a microalloyed AISI 304L stainless steel was investigated by the advanced thermomechanical process of reversion of strain-induced martensite. For this purpose, samples were subjected to heavy cold rolling to produce a nearly complete martensitic structure. Subsequently, a wide range of annealing temperatures (600 to 800°C) and times (1 to 240 min) were employed to assess the reversion behavior and to find the best annealing condition for the production of the nano/ultrafine grained austenitic microstructure. Microstructural characterizations have been performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and magnetic measurement, whereas the mechanical properties were assessed by tensile and hardness tests. After thermomechanical treatment, a very fine austenitic structure was obtained, which was composed of nano sized grains of ~ 85 nm in an ultrafine grained matrix with an average grain size of 480 nm. This microstructure exhibited superior mechanical properties: high tensile strength of about 1280 MPa with a desirable elongation of about 41%, which can pave the way for the application of these sheets in the automotive industry.

Keywords: *austenitic stainless steel, martensite reversion, nanomaterials, phase transformations.*

1. Introduction

Austenitic stainless steels (ASS) are extensively used in various applications requiring good corrosion resistance and formability. Meanwhile, the development of high strength steels characterized by a combination of high strength and ductility continues to be a major field of study [1]. In this regard, grain refinement dominates the efforts to achieve this objective. These steels do not undergo a considerable grain refinement by recrystallization process and the level of grain refinement achieved is limited to a few micrometers [1]. The heuristic processing route of controlled reversion annealing of the heavily cold-deformed martensite in metastable Cr-Ni austenitic stainless steels has been introduced for production of highly refined austenitic structures [2-5]. In the first stage, the deformation of austenite at a sufficiently low temperature leads to the formation of strain-induced martensite (SIM). Tomimura et al. [4] stated that a nearly complete martensitic structure is essential for the achievement of nano/ultrafine grained (N/UFG) structure in subsequent reversion annealing. Two types of martensite phases can be formed during deformation: the HCP ε-martensite and BCC α'-martensite [5-9]. The mechanisms of martensitic transformation have been extensively studied and it has been established that α'-martensite nucleates at the intersections of shear bands that consist of ε-martensite, stacking fault bundles and mechanical twins [1]. The amount of α'-martensite increases with increase in plastic strain at the expense of austenite and ε-martensite phases using the following mechanisms: $\gamma \rightarrow \alpha'$ and $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ [10-11]. In the second stage, on annealing, the heavily deformed martensite is transformed into fine-grained austenite either through a martensitic shear or diffusional reversion mechanism [4]. Therefore, an accurate annealing schedule to inhibit grain growth leads to the formation of N/UFG structure [5].

Figure 1 summarizes the pictorial representation of the thermomechanical process used to obtain a Nano/ultrafine grained austenitic structure through controlled reversion of SIM in metastable ASS. This study is based on the thermomechanical treatment of ASSs containing a considerable amount of microalloying elements. The advantage of using these elements is seen in their pinning effect, which may interfere with the grain growth during the reversion treatment and hence brings about the possibility of achieving a finer microstructure after reversion.

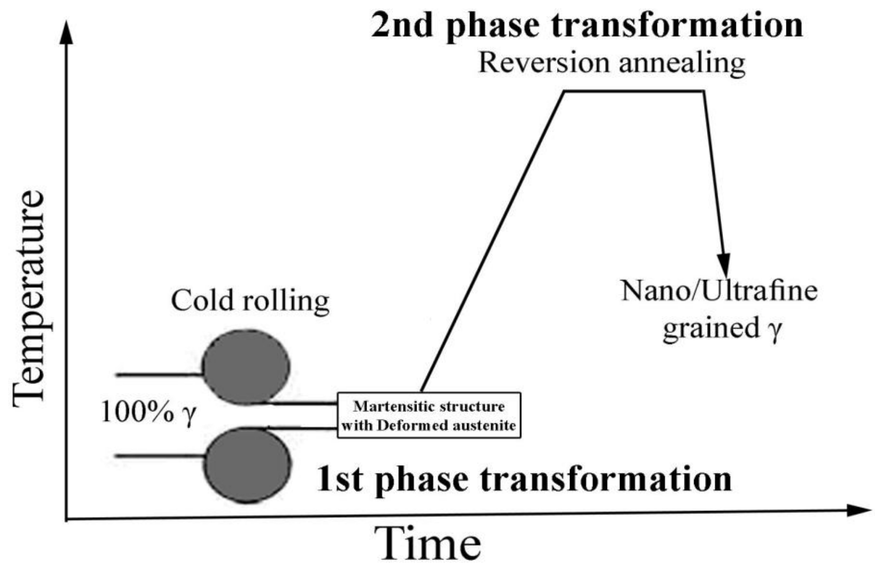


Fig. 1. Schematic of advanced thermomechanical process used to obtain Nano/ ultrafine grained austenitic stainless steel [4]

2. Experimental

Commercial type 304L stainless steel with chemical composition shown in Table 1 was used in this study. The XRD analysis was performed using a Philips PW-3710 diffractometer with Cu Kα radiation on the as-received material and the result is shown in Figure 2a. The optical microstructure shown in Figure 2b exhibits equiaxed grains with average intercept length of 10 µm. The specimens were subjected to cold rolling at room temperature to achieve reductions in thickness (equivalent strains) of 25% (0.370), 35% (0.590), 45% (0.707), 55% (0.922) and 65% (1.103). To characterize the microstructural details, electro-etching was carried out in 60% HNO_3 solution at 2 V [12] to reveal austenite grains. For evaluation of mechanical properties, tensile tests were performed at room temperature using a universal materials testing machine operating under a strain rate of $10^{-3}s^{-1}$. The tensile test specimen was in accordance with the subsize ASTM E-8 standard.

Table 1. Chemical composition (wt.%) of the investigated material

Element	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Ti	V	Nb	Fe
Wt%	0.023	0.476	1.430	0.019	0.0002	0.110	18.470	8.050	0.089	0.003	0.129	0.128	Bal.

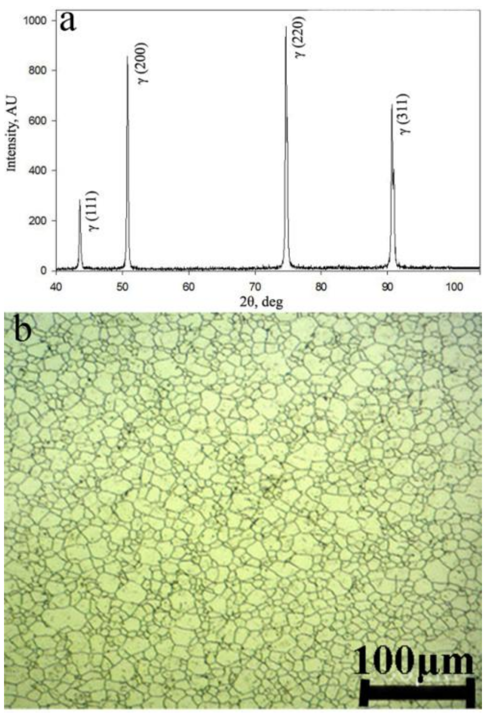


Fig. 2. a) X-ray diffraction pattern of the as-received material, b) the corresponding optical micrograph

3. Results and Discussion

3.1. Formation of strain-induced martensite

The stability of austenite in terms of $Md_{30/50}$ temperature (The temperature at which 50% martensite is formed by applying equivalent strain of 0.3) as proposed by Angel [13] was found to be 55°C (based on Eq.1), which is sufficiently above room temperature, and the Ms temperature calculated according to Eichelmann and Hull equation [1] is -60.65°C (according to Eq. 2), which is well below the room temperature. Therefore, the studied material probably fulfills the basic pre-condition for austenitic metastability and formation of SIM during cold rolling.

$$M_{d30/50}(°C)=413-[462\ (\%C+\%N)+9.2\ (\%Si)+8.1\ (\%Mn)+13.7\ (\%Cr)+9.5\ (\%Ni)+18.5\ (\%Mo)] \quad (1)$$

$$M_s(°C)=1305-[1667\ (\%C+\%N)+28\ (\%Si)+33\ (\%Mn)+42\ (\%Cr)+61\ (\%Ni)] \quad (2)$$

The volume fraction of α'-martensite, derived by the direct comparison method [1], as a function of total cold reduction at room temperature is depicted in Figure 3. It can be seen that the austenite phase (γ) has not been completely transformed into α'-martensite phase by applying 65% cold reduction. Therefore, a lower temperature of ~ 10°C was employed for rolling, which resulted in higher amount of α'-martensite (91%), as a result, this microstructure was used in subsequent reversion annealing.

The stacking fault energy (SFE) is a key factor in specifying the dominant mechanism for the formation of SIM in the following manner. The formation of SIM has been attributed to shear bands, which are planar defects that are related to the overlapping of stacking faults on {111} γ [1]. It has been reported that the lower stacking fault energies lead to the transformation sequence of $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ [14-15]. The stacking fault energy (SFE) of the investigated material has been estimated as 15.25 mJ.m^{-2} using the following equation [16]:

$$SFE\,(mJ.m^{-2}) = -53 + 6.2(Ni) + 0.7(Cr) + 3.2(Mn) + 9.3(Mo)(Wt\%) \quad (3)$$

Subsequently, according to the predicted values of SFE for the investigated material, it is expected that the transformation sequence of $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ becomes the dominant one in this study. To evaluate this speculation, the XRD analysis was performed on a slightly rolled sample to an equivalent strain of 0.1 at ~ 10°C (Fig. 4). A qualitative inspection of this figure clearly demonstrates the presence of ε-martensite peaks. It can thus be mentioned that a transformation of the type $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ has been underway.

3.2. Reversion of strain-induced martensite

The exposure of martensitic structure at elevated temperature leads to the formation of reverted austenitic structure. In this regard, the amount of reverted austenite is directly related to the soaking time and temperature. A substantial prerequisite for grain refinement by reversion of α'-martensite is the near complete reversion of SIM into the austenite phase after annealing treatment. Figure 5 illustrates the effect of annealing temperature and time on the amount of SIM. It can be seen that by increasing the annealing temperature or time, the amount of reverted austenite will increase but the effect of annealing temperature is more significant than that of annealing time. However, higher temperatures increase the grain growth rate, which adversely affect the obtained fine microstructure.

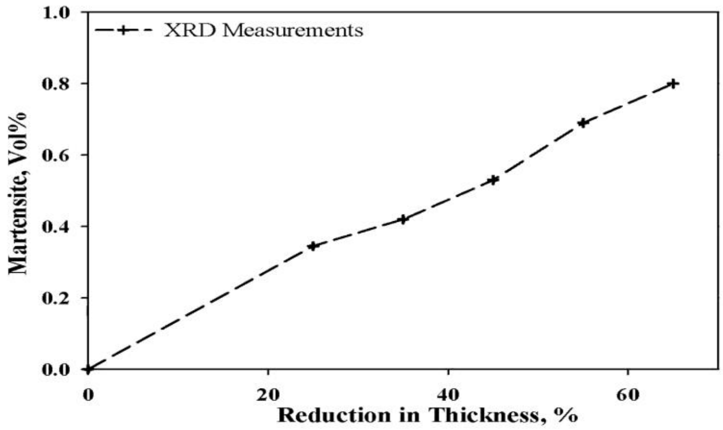


Fig. 3. Volume fraction of α'-martensite as a function of cold reduction in AISI 304L ASS at 25 °C

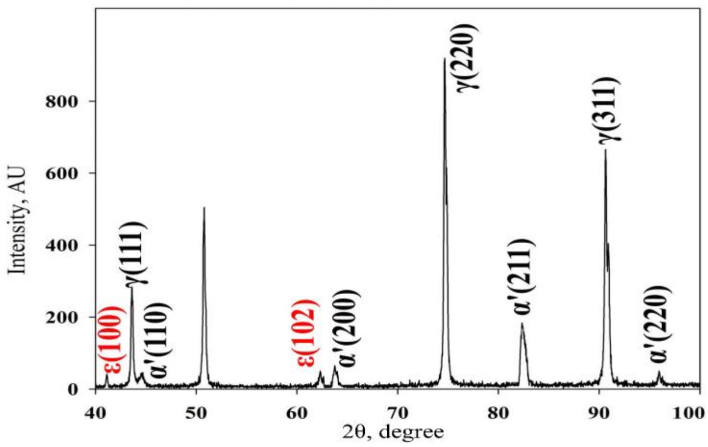


Fig. 4. X-ray diffraction pattern of the cold rolled (10 °C) AISI 304L stainless steel

Shirdel et al. [12] and Shirdel et al. [17] have studied the effect of annealing time and temperature on the grain growth behavior of the same material. Accordingly, the growth rate was found to dramatically increase at temperatures higher than 800°C. Based on this result and by considering the results of Figure 5, for the determination of nearly full reverted austenitic microstructures, the specimen annealed at 650°C for 240 min was selected as the best candidate for further analysis.

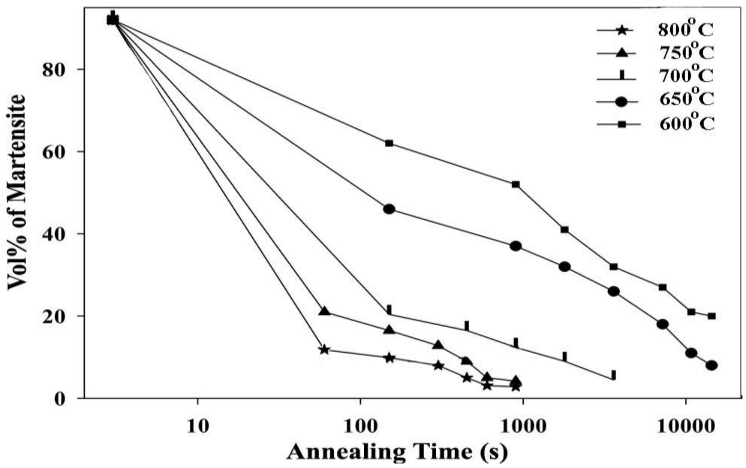
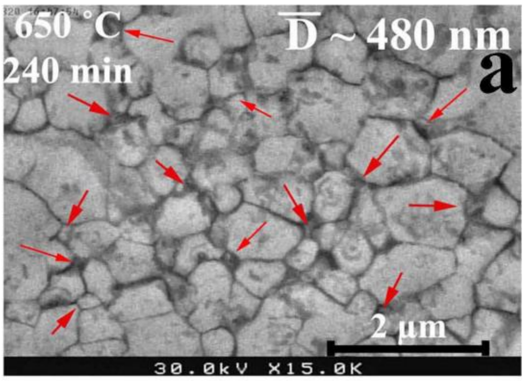


Fig. 5. Vol% of Martensite *vs.* annealing time at various reversion temperatures as determined by magnetic measurements

The SEM image taken from the microstructure of the mentioned sample is shown in Figure 6. Red arrows indicate the nano sized austenite grains (~85 nm). Its corresponding grain size distribution histogram has also been plotted to obtain a better quantitative view from the resultant microstructure. This interesting result shows that the thermomechanical process of SIM reversion can be regarded as an important and applicable process for achievement of Nano/UFG structure in AISI 304L ASS. Di Schino et al. [18] reported that the smallest average grain size obtained by reversion of SIM for AISI 304 stainless steel is about 800 nm. The smaller average grain size of UFG austenite obtained in the present investigation may be attributed to the slower grain growth kinetics due to the presence of microalloying elements.

Grain refining is commonly known to raise the strength and hardness of polycrystalline materials [3,19]. Table 2 summarizes the comparative results of mechanical evaluations of the studied material. Obviously, a significant improvement of the mechanical properties was obtained; the yield strength and tensile strength increased to 940 and 1280 MPa from the initial values of 273 and 543 MPa, respectively; the ductility was not deteriorated and it reached an acceptable value of 41%. Also, the heavily cold rolled sample is characterized by a severe increase of strength with consequent lowering of percent elongation.



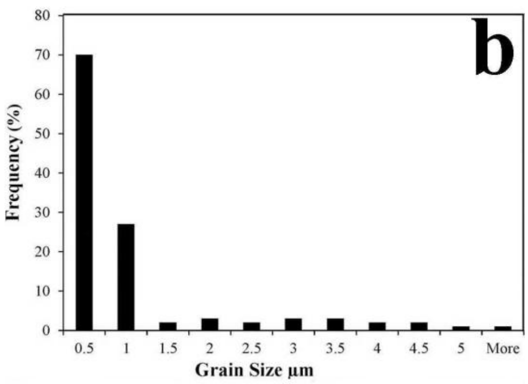


Fig. 6. SEM image taken from the microstructure of sample annealed at 650°C for 240 min, and the corresponding grain size histogram

Table 2. The phase percentage, grain size, and mechanical properties of the specimens after different processing condition

Processing Condition	Structure	$\overline{D}$	σ_y MPa	σ_{UTS} MPa	Fracture Strain%	Hardness HV
As-received	~ 100 % γ	~10 μm	273	543	51	161
65% CR at 283K+923K/240 min	~ 98 % γ	~ 480 nm	940	1280	41	560
65% CR at 248K	~ 98 % α'	-	1965	1997	10	710

4. Summary and conclusions

A microstructure consisting of nano-sized grains (~85 nm) in an ultrafine grained matrix with an average grain size of 480 nm was obtained through the martensite treatment of Type 304L ASS. It was shown that cold rolling at a temperature of 25°C could not lead to the production of required amount of martensite (~>90%). Therefore, a fall in temperature to about 10°C seems to be sufficient for successful subsequent annealing to produce nano/ultrafine grained microstructure. The data revealed a considerable effect of grain refinement on the mechanical properties of the 304L ASS and the ultimate tensile strength of the order of 1280 MPa accompanied with a high ductility of ~ 41% was achieved by this thermomechanical treatment.

References

[1]. Lo, K. H., Shek, C. H., Lai, J. K. L., Mater. Sci. Eng. R Vol. 65 (2009) pp. 39–104.

[2]. Lee, S. J., Park, Y. M., Lee, Y. K., Mater. Sci. Eng. A Vol. 515 (2009) pp. 32–7.

[3]. Johannsen, D. L., Kyrolainen, A., Ferreira, P. J., Metal. Mater. Trans. A Vol. 37 (2006) pp. 2325–38.

[4]. Tomimura, K., Takaki, S., Tanimoto, S., Tokunaga, Y., ISIJ Int. Vol. 31 (1991) pp. 721–7.

[5]. Mirzadeh, H., Najafizadeh, A., Mater. Character. Vol. 59 (2008) pp. 1650–54.

[6]. Weidner, A., Hangen, U. D., Biermann, H., Phil. Mag. Lett. Vol. 94 (2014) pp. 522–30.

[7]. Moallemi, M., Najafizadeh, A., Kermanpur, Rezaee, A., Mater. Sci. Eng. A Vol. 530 (2011) pp. 378–81.

[8]. Eskandari, M., Najafizadeh, A., Kermanpur, A., Karimi, M., Mater. Des. Vol. 30 (2009) 3869-3872.

[9]. Mirzadeh, H., Najafizadeh, A., Mater. Des. Vol. 30 (2009) pp. 570–3.

[10]. Ma,Y., Jin, J. E., Lee, Y. K., Mater. Sci. Forum Vol. 475 (2005) pp. 43–48.

[11]. Somani, M. C., Juntunen, P., Karjalainen, L. P., Misra, R. D. K.,Kyrolainen, A., Metal. Mater. Trans. A Vol. 40 (2009) pp. 739–44.

[12]. Shirdel, M., Mirzadeh, H., Habibi Parsa, M., Metall. Mater. Trans. A Vol. 45 (2014) pp. 5185–93.

[13]. Angel, T., J. Iron and Steel Inst. Vol. 177 (1954) pp. 165–74.

[14]. Olson, G. B., Cohen, M., Metal. Trans. A Vol. 6 (1975) pp. 791–5.

[15]. Huang, G. L., Matlock, D. K., Krauss, G., Metal. Mater. Trans. A Vol. 20 (1989) pp. 1239–46.

[16]. Schramm, R. E., Reed R. P., Metal. Mater. Trans. A Vol. 6 (1975) pp. 1345–51.

[17]. Shirdel, M., Mirzadeh, H., Habibi Parsa, M., Mater. Charact. Vol. 97 (2014) pp. 11–7.

[18]. Di Schino, A., Salvatori, I., Kenny, J. M., J. Mater. Sci. Vol. 37 (2002) pp. 4561–66.

[19]. Chen, M., Ma, E., Hemker, K. J., Sheng, H., Wang, Y., Cheng, X., Science Vol. 300 (2003) pp. 1275–7.