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The grain size and special boundary dependence of corrosion resistance in 304 austenitic stainless steels

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HIGHLIGHTS

- The cryogenic cold deformation facilitated grain refinement and reduced fraction of CSL.
- The grain refinement accelerated sensitization, even though the ratio of CSL increase.
- Higher DOS reduced corrosion resistance of 304 austenitic stainless steel.

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ABSTRACT

The effect of cold rolling temperature on grain boundary characteristic of the 304 austenitic stainless steels in thermomechanical treatment was examined. Comparing to cold rolling at room temperature and annealing, the cryogenic cold deformation and annealing promoted grain refinement and reduced fraction of coincidence site lattice. Although more coincidence site lattice restrained sensitization, the grain refinement accelerated sensitization. The sensitization deteriorated corrosion resistance of 304 austenitic stainless steel obtained by thermomechanical treatment.

1. Introduction

The concept of grain boundary design and control was developed as grain boundary engineering (GBE) [1]. Grain boundary coincidence site lattice (CSL) boundaries were resistant to intergranular deterioration processes [2] and stress corrosion cracking [3]. This was mainly attributed to the lower free energy of special boundary [4]. The twin boundaries formed in the surface of mechanical attrition treated sample weren't susceptible to carbide precipitation because of their regular and coherent atomic structure and extreme low grain boundary energy compared with those of other grain boundaries [5]. However, recently, Nie et al [6] reported an unusual phenomenon in magnesium alloys and the equilibrium segregation of solute atoms formed in coherent deformation twin boundaries. The grain boundary related properties were greatly enhanced by the frequency of CSL which was greatly increased by using proper thermo-mechanical treatments [7]. A notable advantage of the GBE process for the 304 stainless steel was obtained by one-step slight strain plus annealing process [8]. A very high frequency of CSL boundaries (86%) was introduced in 316 austenitic stainless steel and the resulting steel showed a remarkably high resistance to intergranular corrosion [9]. An attempt was made to correlate the degree of sensitization (DOS) with various microstructural parameters such as grain size and grain boundary nature in AISI 316LN austenitic stainless steel. No clear trend could be established between the individual parameters and DOS, while effective grain boundary energy (EGBE) showed clear trend with DOS [10]. The grain size also affects the subsequent performance of thermo-mechanical treatments. The study on measuring the sensitization rates and $M_{23}C_6$ precipitation behavior

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over a range of grain sizes from 15 to 150 μm in 304 stainless steel also showed that the sensitization process was accelerated as the grain size decreased [11].

The cellular automaton simulation indicated that the precipitation of Cr-rich carbides in the large grain microstructure was less than that in the small grain microstructure [12]. Li et al. [13] found that chromium carbide precipitations were much delayed in larger grains in 316L stainless steel and the DOS decreased with the increasing of grain size.

At present an important purpose of the research GBE is tailoring optimized grain size and grain boundary characteristic to inhibit the formation of chromium rich carbides and improve corrosion resistance of austenitic stainless steel. The objective of the present work was to study the effect of cold rolling temperature on grain boundary characteristic distribution and grain size in thermo-mechanical treatment and corrosion resistance of 304 austenitic stainless steels.

2. Experimental

The material used in this paper is a 304 stainless steel plate with a chemical compositions (wt.%) as follows: 0.05 C, 1.44 Mn, 0.6 Si, 17.8 Cr, 9.1 Ni, 0.035 P, 0.002 S, and balance Fe. The 8 mm sheet was solid solution annealed in 1050 °C for 1 h in a vacuum tube and quenched in water to achieve chemical homogeneity. Some samples were rolled to 20% thickness reduction at room temperature. Cryogenic deformation was carried out after the sample was immersed in liquid-nitrogen and sample also was rolled to 20% thickness reduction. Then cold rolled samples were annealed in 950 °C for 20 min. The samples for sensitization were heat-treated at 675 °C for 2 h following water quenching.

The frequency of CSL boundaries and grain boundary characteristic distribution (GBCD) were in ZEISS ULTRA 55 field emission gun SEM equipped with an HKL Technology Channel 5 EBSD detector. The frequency of CSL boundaries was cited as a percentage by length on the cross-section. Brandon's criterion [14] was adopted for the critical deviation in the grain boundary characterization [15]. In the present study, grain boundaries with $\sum \leq 29$ were classified as CSL boundaries with low energy, the others being classified as random boundaries with high energy [16]. Cu Kα (0.154056 nm) radiation at 40 kV and 40 mA at 4°/min was used for X-ray diffraction (Rigaku Ultima IV) analysis.

The samples were polished with 1000, 2000 and 3000 grit silicon carbide paper and 1.5 μm alumina slurry. The polished samples were ultrasonically cleaned in acetone and ethanol. Very high density graphite and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All the potentials referred in this work were measured with respect to the value of SCE. Before each experiment the samples were cathodically polarized at −1.2 V_{SCE} for 300 s. The electrochemical measurements were performed using CHI660B electrochemical station (Chenhua instrument Co. Shanghai, China) controlled by computer and software.

The role of KSCN was to help to break the passive film during the reactivation cycle of the test. The double loop electrochemical potentiokinetic reactivation technique (DLEPR) was conducted using 0.5 M H_2SO_4 + 0.01 M KSCN solution [17]. The DLEPR experiments were started after nearly steady state open circuit potential (OCP) had been reached (about 30 min), and the potential swept in the anodic direction at 1 mV s^{-1} until the potential of 0.3 V_{SCE} was reached, then the scan was reversed until the OCP.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in 3.5% NaCl solution at −0.2 V_{SCE} for 1 h using a frequency range of 100 kHz–10 mHz and with a 5 mV amplitude of the ac signal.

3. Results and discussion

The microstructures shown in Fig. 1a–c exhibit equiaxed grains characteristic of stainless steels after different thermo-mechanical treatments. The average sizes of solid solution annealed sample, room temperature rolling and cryogenic rolling and annealed samples are shown in Fig. 2. Deformation in lower temperature promoted α′-martensite transformation of austenitic stainless steel [18] and grain refinement [19]. Wang et al. [20] reported that the deformation of 1Cr18Ni9Ti stainless steel at liquid-nitrogen temperature had a positive effect on developing high-angle boundaries and grain refinement. More strain induced α′-martensites in cryogenic rolled sample in Fig. 1d promote grain refinement during reversed transformation by annealing.

Fig. 2 shows that the influence of the different thermo-mechanical treatments on CSL. Firstly, Overall, the cold deformation and annealing significantly increase fraction of CSL. Secondly, the cryogenic cold deformation and annealing reduces fraction of CSL.

Several methods can be used to improve ratio of CSL, firstly, reducing the stacking fault energy of materials. Secondly, reducing the deformation temperature, Thirdly, increasing the deformation rate. Fourthly, improving the thermal stability of deformation twins. In the present thermomechanical treatments, although low temperature rolling promotes deformation twins, high storage energy after cryogenic cold deformation facilitates movement of the twin boundary, which decreases ratio of CSL in the study.

In face-centered cubic metal with high stacking fault energy, high ratio of CSL can be obtained by small deformation and high temperature annealing. As far as we know, the high proportion of CSL (above 80%) is only obtained in coarse grained metal. In the present study, the medium cold rolled level is used, which results in refined grain in the subsequent annealing process. Previous studies have suggested that grain refinement can improve the stacking fault energy, which inhibits the formation of high ratio of CSL. It is worth noting that nanotwins can only be formed in metal with the low stacking fault energy (for example, copper). However, stacking fault energy of austenitic stainless steel is medium level. Therefore, proportion of CSL is less than 80%. However, it is very significant to study the effect of the CSL ratio in the refined austenitic stainless steel on its the mechanical properties and corrosion resistance.

Dependencies between current and potential are obtained on the base of the DLEPR measurements in Fig. 3a. The significant activation and reactivation peaks can be observed. The magnitude of the DOS is shown in Fig. 3b. Compared with solid solution sample, the grain size of sample by thermal mechanical process reduces by 64.6% and 79.69% for # 2 and # 3 samples, while CSL increases by 177% and 130%. The DOS increases by 36.11% and 94%, respectively. This means that grain refinement accelerates sensitization, even though the ratio of CSL increases.

The EIS measurements were performed at −0.2 V_{SCE} after sample is passivated for 1 h in 3.5% NaCl solution. The Nyquist plots in Fig. 4a are all composed of depressed semicircles. The smallest semicircle indicates deteriorated property of the passive film. A significant decrease of semicircle is observed in sample with the largest DOS. It is evident that a time constant appears on the basis of peak value of phase angle in Fig. 4b. The capacitive semiarc of # 1 sample is much larger than those of # 2 and # 3 samples. In contrast, the capacitive semiarc of # 3 sample is much smaller than that of # 2 sample. The EIS results are in good agreement with DOS, which indicates that the corrosion resistance of grain refined sample decreases in this solution.

Fig. 5a shows Mott–Schottky plots for the passive films formed on # 1 # 2 and # 3 samples in 3.5% NaCl solution. The passive film was formed at −0.2 V_{SCE} for 1 h. The results show that there are