INTERGRANULAR CORROSION-RESISTANT STAINLESS STEEL BY GRAIN BOUNDARY ENGINEERING

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ABSTRACT

Intergranular corrosion of austenitic stainless steels is a conventional and momentous problem during welding and high temperature use. One of the major reasons for such intergranular corrosion is so-called sensitization, i.e., chromium depletion due to chromium carbide precipitation at grain boundaries. Conventional methods for preventing sensitization of austenitic stainless steels include reduction of carbon content in the material, stabilization of carbon atoms as non-chromium carbides by the addition of titanium, niobium or zirconium, local solution-heat-treatment by laser beam, etc. These methods, however, are not without drawbacks. Recent grain boundary structure studies have demonstrated that grain boundary phenomena strongly depend on the crystallographic nature and atomic structure of the grain boundary, and that grain boundaries with coincidence site lattices are immune to intergranular corrosion. The concept of "grain boundary design and control", which involves a desirable grain boundary character distribution, has been developed as grain boundary engineering. The feasibility of grain boundary engineering has been demonstrated mainly by thermomechanical treatments. In the present study, a thermomechanical treatment was tried to improve the resistance to the sensitization by grain boundary engineering. A type 304 austenitic stainless steel was pre-strained and heat-treated, and then sensitized, varying the parameters (pre-strain, temperature, time, etc.) during the thermomechanical treatment. The grain boundary character distribution was examined by orientation imaging microscopy. The intergranular corrosion resistance was evaluated by electrochemical potentiokinetic reactivation and ferric sulfate-sulfuric acid tests. The sensitivity to intergranular corrosion was reduced by the thermomechanical treatment and indicated a minimum at a small roll-reduction. The frequency of coincidence-site-lattice boundaries indicated a maximum at a small strain. The ferric sulfate-sulfuric acid test showed much smaller corrosion rate in the thermomechanically-treated specimen than in the base material. An excellent intergranular corrosion resistance was obtained by a small strain annealing at a relatively low temperature for long time. The optimum parameters created a uniform distribution of a high frequency of coincidence site lattice boundaries in the specimen where corrosive random boundaries were isolated. The results suggest that the thermomechanical treatment can introduce low energy segments in the grain boundary network by annealing twins and can arrest the percolation of intergranular corrosion from the surface.

KEYWORDS

Austenitic stainless steel, Grain boundary engineering, Intergranular corrosion, Grain boundary structure, Orientation imaging microscopy

1. Introduction

Chromium depletion due to chromium carbide precipitation at grain boundaries, i.e., sensitization in austenitic stainless steels can not be prevented perfectly only by conventional techniques, such as reduction of carbon content, stabilization-treatment, solution-heat-treatment, etc.[1]. Grain boundaries with low-Σ coincidence site lattices (CSLs) are immune to intergranular corrosion [2-6]. The concept of 'grain boundary design and control' [7] has been developed and refined as grain boundary engineering (GBE) [8-10]. GBEed materials are characterized by high frequencies of CSL boundaries which are resistant to intergranular deterioration of materials, such as intergranular corrosion [6,8]. The feasibility of GBE has been demonstrated mainly by thermomechanical treatments, which can be broadly divided into strain recrystallization and strain annealing processes [4,5,10-16]. Palumbo et al. have improved the intergranular corrosion susceptibility in nickel base alloys by the strain recrystallization process [4,5,8,10], while King et al. have reported evolution of the grain boundary character distribution (GBCD) in Cu by the strain annealing process [12,14]. Generation of $\Sigma 3^n$ CSL boundaries by twin events [17] during thermomechanical treatment can increase the frequency of CSL boundaries in the materials, but may not always result in the optimum GBCD. The effects of parameters such as pre-strain, temperature and time in the thermomechanical treatment on the GBCD during GBE are as yet unclear, since the parameters differ between researchers. The authors have examined the effects of the parameters in the thermomechanical treatment on the GBCD and intergranular corrosion of 304 stainless steel [1,18,19]. The optimization of parameters and favorable GBCD in grain boundary engineering for intergranular corrosion resistant stainless steel were discussed in this paper by reviewing our recent study [1,18,19].

2. Experimental procedures

A type 304 austenitic stainless steel was used as the base material (BM). The chemical composition (wt%) is 18.28 Cr, 8.48 Ni, 0.60 Si, 1.00 Mn, 0.055 C, 0.029 P, 0.005 S. The initial size of the base material specimen was 9x10x35mm. The specimens were solution-heat-treated at 1323 K for 0.5 h. Pre-stain before annealing was achieved by cold-rolling. The roll reduction ratio in thickness was varied from 0 to 60%. The pre-strained specimens were annealed at 1200, 1300 and 1400 K and quenched in cold water. The GBCD was examined by orientation imaging microscopy (OIM). In this study, grain boundaries with $\Sigma \leq 29$ were regarded as low-Σ CSL boundaries, and Brandon's criterion [20] was adopted for the critical deviation in the grain boundary characterization [21]. The intergranular corrosion resistance was evaluated by a double loop electrochemical potentiokinetic reactivation (DL-EPR) test [22] after sensitization treatment at 923K for 1 h. The base material (BM) and 5% strain-annealed (r5%) specimens were assessed by a ferric sulfate-sulfuric acid test [23] after sensitization at 923 K for 2 h. The tested specimens were observed by scanning electron microscopy (SEM).

3. Results and discussion

OIM observations of the specimens thermomechanically treated at 1300 K indicated the effect of the roll reduction ratio on the frequency of CSL boundaries as shown in Figure 1. The frequency of CSL boundaries showed the maximum at 5% reduction, while higher reduction rates did not result in high frequency of CSL boundaries. Figure 2 shows the effect of the roll reduction ratio on the reactivation current ratio during the DL-EPR test after sensitization. As the degree of sensitization (DOS) is indicated by the reactivation current ratio, a lower current ratio means smaller sensitization. The DOS of the thermomechanically treated specimen was reduced compared with the value of the BM, and the minimum DOS was seen at 5% reduction, which is consistent with the maximum frequency of CSL boundaries at 5% reduction in Figure 1 in the consideration that higher CSL frequency leads to higher corrosion resistance. Figures 1 and 2 revealed that a small pre-strain around 5% before annealing at 1300 K resulted in a minimum degree of sensitization (DOS) during the DL-EPR test and a maximum in the frequency of CSL boundaries in the sensitized specimen. Thus, the optimum degree of pre-strain around 5% was examined by varying roll-reduction in small steps within 10%.

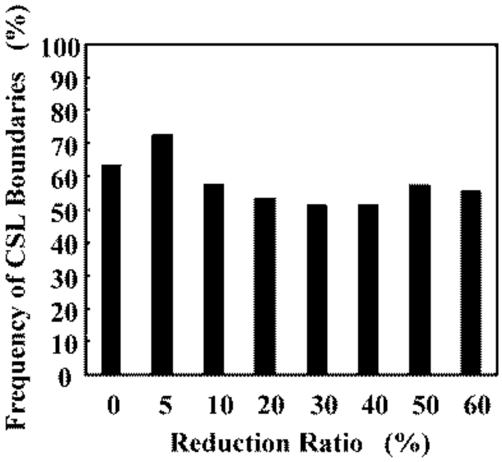

Fig. 1 Roll reduction and frequency of CSL boundaries.

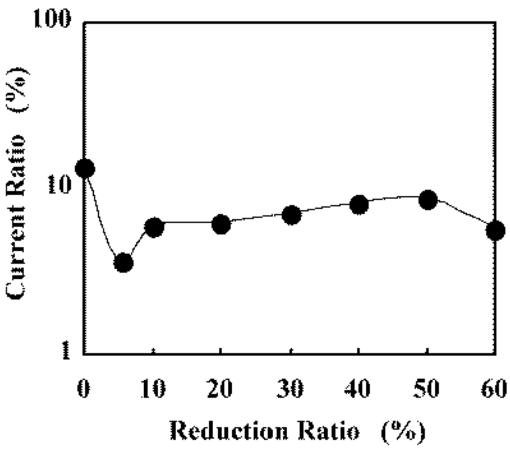

Fig. 2 Roll reduction and EPR test result.

The DL-EPR test result as shown in Figure 2 reflects the fractional area of chromium depletion near sensitized grain boundaries on the test surface. The actual intergranular corrosion propagates along grain boundaries from the surface into the material and causes mass-loss due to grain dropping. The corrosion (mass-loss) rate during the ferric sulfate-sulfuric acid test is shown for the BM and an r5% specimen in Figure 3. The r5% specimen has a much smaller corrosion loss than the BM for every test-duration. The difference in mass-loss between the BM and the r5% specimen is much more than that expected from Figures 1 and 2. The specimen surfaces after the ferric sulfate-sulfuric acid test showed more remarkable grain dropping due to intergranular corrosion in the BM than that in the r5% specimen. After DL-EPR and ferric sulfate-sulfuric acid tests, non-corroded parts in the corroded grain boundaries from where annealing twins were emitted were frequently observed in the r5% specimen, as shown in Figure 4(a). The OIM image in Figure 4(b) suggests that the non-corroded part in Figure 4(a) transformed the grain boundary structure from random to Σ29a CSL by twin emission. OIM observation of the r5% specimen revealed that some but not all of the non-corroded parts in the corroded random boundaries were of low-Σ CSL misorientations.

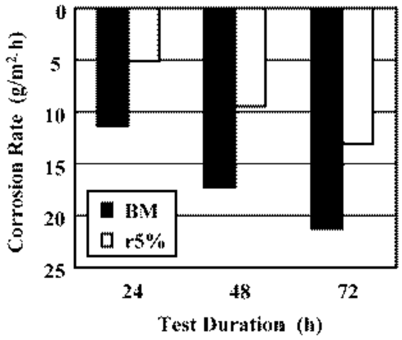

Fig. 3 The corrosion mass-loss of r5% specimen.

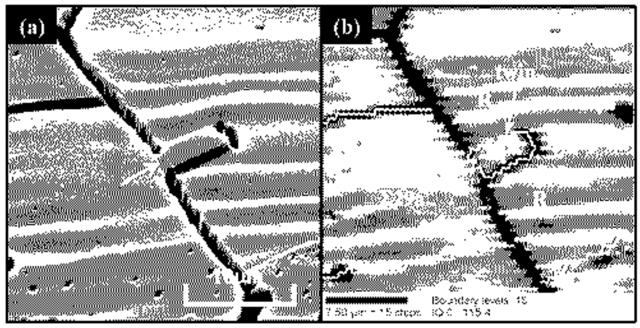

Fig. 4 Annealing twin by SEM (a) and OIM (b).

Since an annealing twin formation generally reduces the grain boundary energy during grain growth [24], the grain boundary energy of the part where the twin was emitted is likely to be lower than that of the initial random boundary. A twin formation can introduce a low energy segment into the random high angle grain boundary and sometimes result in low-Σ CSL structures as shown in Figure 4. Active twin events and reactions increase the frequency of CSL boundaries and also produce low energy segments in high energy boundaries locally and frequently during thermomechanical treatment of low stacking fault energy materials such as 304 austenitic stainless steel. Well-distributed low energy segments in the grain boundary network create a discontinuous chain of chromium depletion and can arrest the percolation of intergranular corrosion from the surface as illustrated in Figure 5. A small pre-strain of around 5% is probably more suitable for an optimum distribution of non-corrosive segments than large pre-strains, because a large pre-strain tends to promote recrystallization generating corrosive random boundaries while a small pre-strain accelerates grain growth accompanying twins during thermomechanical treatment.

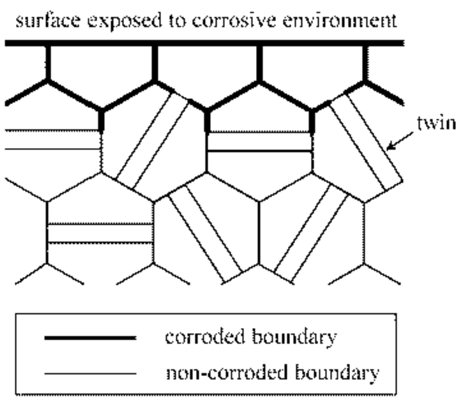

Fig. 5 Arrest mechanism of intergranular corrosion.

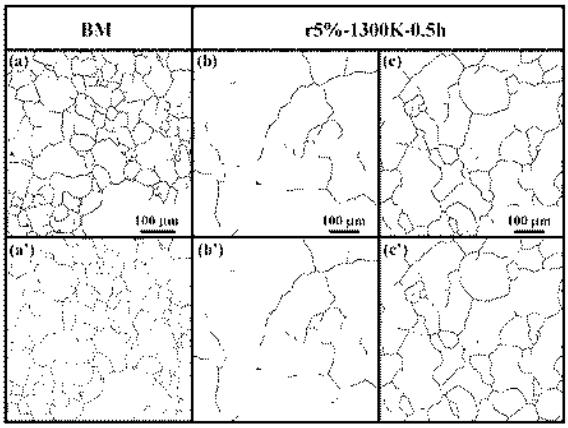

Fig. 6 Grain boundary character distributions by OIM.

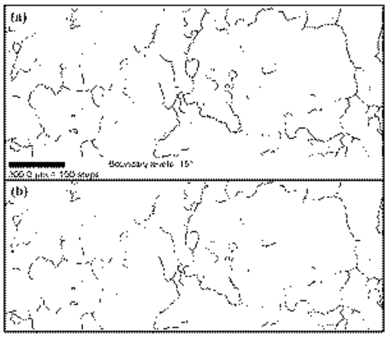

Fig. 7 GBCD of r5%-1200K-72h by OIM.

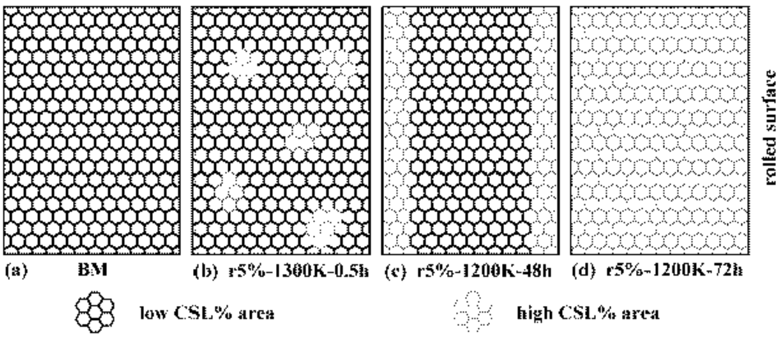

Fig. 8 Schematic GBCD change by thermomechanical treatment.

The effect of annealing temperature at 5% pre-strain on the grain boundary character distribution (GBCD) was examined by OIM. Figure 6 shows OIM images of the BM and r5% specimens annealed at 1300 K and 1200 K. Random and CSL boundaries are indicated by thick black and thin gray lines, respectively, in Figure 6(a). Figure 6(b) showed only the lines of random boundaries in Figure 6(a). A continuous network of random boundaries was uniformly developed in the BM, where the frequency of CSL boundaries is about 63%. The r5% specimen annealed at 1300 K (r5%-1300K) had an average frequency of CSL boundaries of about 75%, but the GBCD was heterogeneous, i.e., areas with high and low frequencies of CSL boundaries coexisted in the specimen. The GBCD of the area with a high frequency of CSL boundaries in the r5%-1300K specimen is shown in Figure 6. The CSL boundary frequency was about 85%. If the higher CSL frequency area in the r5%-1300K specimen were to spread thoroughly throughout the specimen, more significant improvement in intergranular corrosion resistance could be expected. The annealing temperature and time were varied to find the process parameters for the optimum GBCD. Annealing at 1400 K brought no different results from those at 1300 K. A uniform distribution of a high CSL frequency area was achieved in the r5% specimen annealed at 1200 K for 72 h (r5%-1200K), as shown in Figure 7. The frequency of CSL boundaries was 86.5% homogeneously in the specimen with a thickness of about 10 mm. The network of random boundaries in the BM was totally disrupted and short random boundary segments were isolated in the r5%-1200K specimen as shown in Figure 7. Kumar et al. [16] attained a discontinuous network of random boundaries in a nickel alloy by more than three cycles of different thermomechanical processes including strain-recrystallization, while a similar GBCD was obtained in a 304 stainless steel by single strain annealing process in the present study. Although frequent twin events and reactions play major roles in the evolution of GBCD during thermomechanical treatment, the active migration of random boundaries may increase opportunities for emission of twins which react with other boundaries, including twins, so as to produce many low-energy segments in original random boundaries without generation of new random boundaries during small-strain annealing at low temperature such as r5%-1200K in this material. The differences in GBCD between the BM, r5%-1300K-0.5h, r5%-1200K-48h and the r5%-1200K-72h specimens are schematically illustrated in Figure 8.

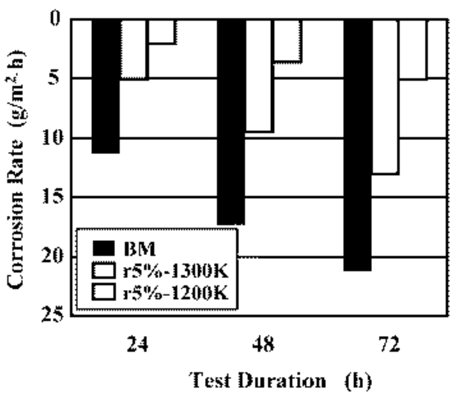

Fig. 9 Corrosion rate of r5%-1200K specimen.

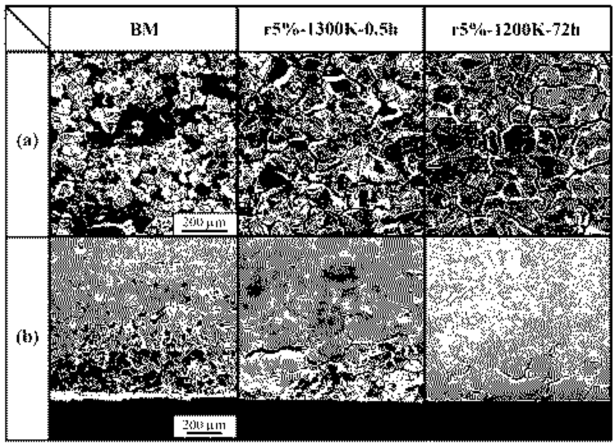

Fig. 10 Corrosion-tested surface and cross-section.

Figure 9 shows the corrosion mass loss rate during the ferric sulfate-sulfuric acid test between the BM, r5%-1300K and r5%-1200K specimens after sensitization. The r5% specimens indicate a much smaller corrosion rate than the BM for every test-duration. Especially, the corrosion rate of the r5%-1200K specimen is less than one fourth that of the BM, and less than half that of the r5%-1300K specimen. The surfaces (Figure 10(a)) and cross sections (perpendicular to the surface) (Figure 10(b)) of the BM, r5%-1300K and r5%-1200K specimens after the ferric sulfate-sulfuric acid test were shown by SEM and are presented in Figure 10. The surface appearances reveal that the grain dropping due to intergranular corrosion was depressed in the r5% specimens, especially in the r5%-1200K specimen. The cross-sectional views also indicate that the penetration of intergranular corrosion from the surface into the material interior was arrested in the r5% specimens, especially in the r5%-1200K specimen.

The intergranular corrosion attacks preferentially random grain boundaries because of selective chromium depletion due to chromium carbide precipitation at random boundaries in austenitic stainless steels [1,6,25]. The high frequency of CSL boundaries and the consequent discontinuous distribution of random boundaries can create high resistance to intergranular corrosion in the material. The excellent corrosion resistance of the r5%-1200K specimen may be the result of the uniform GBCD with a high frequency of CSL boundaries. The intergranular corrosion resistance was remarkably improved by optimization of GBCD during suitable strain annealing.

4. Conclusion

A small strain annealing at a relatively low temperature for long time in thermomechanical treatment demonstrated an excellent resistance to intergranular corrosion of 304 stainless steel during DL-EPR and ferric sulfate-sulfuric acid tests. The optimum parameters in the grain boundary engineering created a uniform distribution of a high frequency of coincidence site lattice boundaries and consequent discontinuity of the random boundary network.

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