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Controlling Grain Boundary Energy to Make Austenitic Stainless Steels Resistant to Intergranular Stress Corrosion Cracking

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Intergranular corrosion and intergranular stress corrosion cracking are the two localized corrosion mechanisms that are of concern to the typical applications of austenitic stainless steels in industries. Until recently, the common understanding was that a higher frequency of random boundaries increases the susceptibility, caused by a sensitization heat treatment or by operating temperatures, of austenitic stainless steels to both intergranular corrosion and intergranular stress corrosion cracking. A recent study[1] demonstrated that extreme randomization of grain boundaries leads to a considerable improvement of resistance to both sensitization and intergranular corrosion. This work is a continuation of Ref. 1 and relates the effects of grain boundary randomization to intergranular stress corrosion cracking: the results show a trend consistent with earlier observations on intergranular corrosion. It is shown that there is improvement in resistance to intergranular stress corrosion cracking with extreme randomization of grain boundaries.

Keywords austenitic stainless steel, corrosion, deformation processing, grain boundaries, intergranular corrosion, intergranular stress corrosion cracking, sensitization stress corrosion cracking

1. Introduction

Austenitic stainless steels (ASS) have excellent resistance to general corrosion. They are, however, prone to localized corrosion like crevice, pitting, intergranular corrosion (IGC), and stress corrosion cracking (SCC). While ASS are inherently prone to transgranular stress corrosion cracking (TGSCC) even in a solution-annealed condition, certain microstructural features can make them prone to intergranular stress corrosion cracking (IGSCC).[2-4] The two forms of localized corrosion, IGC and IGSCC, are directly caused by sensitization.[5] Sensitization is typically found when a stainless steel is welded or heat treated in the temperature range of 500-800 °C. This leads to precipitation of chromium rich carbides at the grain boundaries. Growth of such carbides can lead to the formation of chromium-depleted zones in the immediate surrounding. When the level of chromium in the depletion regions falls below 12-13 wt.%, the passive film over the depleted regions weakens and breaks easily in contact with aggressive solutions. This makes the sensitized ASS prone to IGC and IGSCC.

The common methods[5] used to control sensitization, hence IGC and IGSCC, are (1) solution annealing (to dissolve chromium rich carbides and erase the chromium depletion regions), (2) lowering the carbon levels (to prevent precipitation of chromium rich carbides), and (3) stabilizing carbon by precipitating it with titanium or niobium. Other than the control of chemistry, sensitization control can also be implemented through optimizing grain boundary nature and grain size.[1,6-11] The former is often distinguished from the coincident site lattice (CSL) concept.[12-15] It is the only practical way, at least presently, to relate experimentally obtained local orientation measurements with grain boundary nature or energy[1], but such classification can be far from exact. For example, a so-called $\Sigma 3$ tilt or twist boundary is identical in its misorientation matrix, but has a large difference in energy. Despite such restrictions, the CSL concept is the best available approach to study grain boundary and its properties. It is to be noted that the CSL theory[12-15] defines Σ as the inverse of the coincident sites at the grain boundary, i.e., $\Sigma 3$ denotes that one out of three atomic sites are coincident. $\Sigma 3$-29 are taken as special boundaries and $\Sigma >29$ are taken as random boundaries. These are usually measured in a scanning electron microscope with an orientation imaging microscopy (OIM) attachment. Until recently, the general understanding was that the presence of random, non-CSL high angle boundaries are detrimental to local corrosion resistance. This generalized concept has been repeatedly highlighted in the published literature, patented products, and processes.[8-11] A recent study introduced an alternative:[1] the presence of a very large fraction of random boundaries was observed to be beneficial in making an ASS resistant to sensitization and IGC. Similar trends in experimental data controlling the nature of grain boundaries to control the resistance to sensitization and IGC were also reported in unrelated studies

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[1] The grain boundary energy may vary widely depending on its exact nature. For example, between special and random high angle boundaries of AISI 304L ASS, an energy difference of 20 to 835 mJ/m^2 can exist.[16]

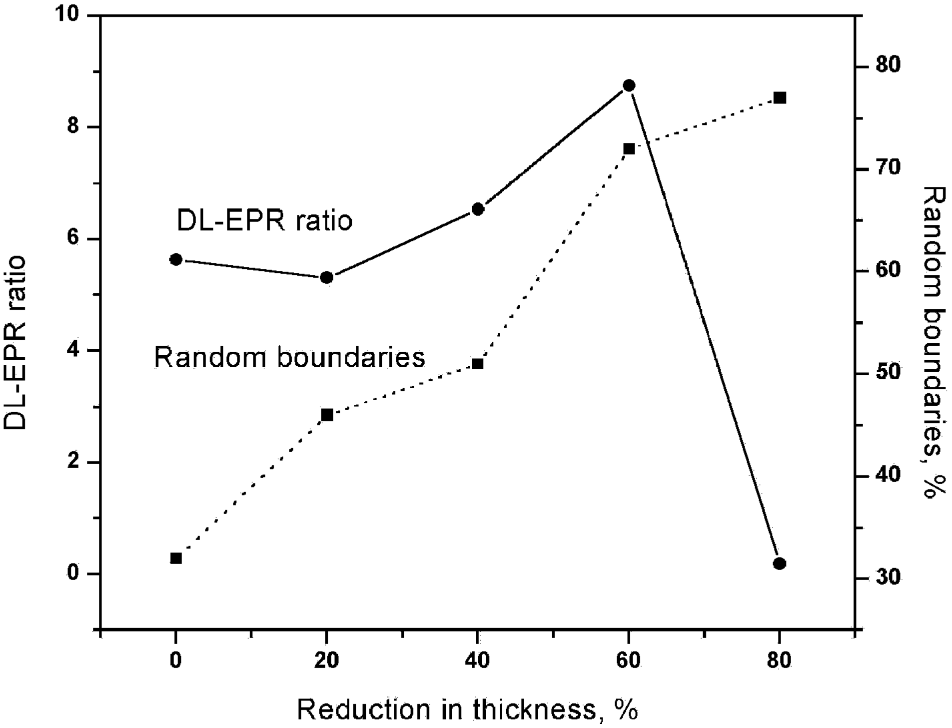

Fig. 1 Plot of DL-EPR ratio and percentage of random boundaries with pre-solutionizing reduction in thickness for type 304 SS, showing significant drop in DL-EPR ratio (or in the Degree of Sensitization, DOS) beyond a "critical" percentage of random boundaries[1]

Table 1 Chemical Compositions, in wt.%, of Type 304 and 316L Austenitic Stainless Steels Used in This Study

Material	C	S	P	Si	Mn	Cr	Ni	Mo	Cu	N
304	0.059	0.010	0.035	0.41	1.43	18.10	8.05	0.09	0.23	0.052
316L	0.025	0.07	0.025	0.46	1.58	17.11	11.69	2.57	0.026	0.027

of another group.[5,6] The current study continues previous research[1] and is aimed at exploring the effects of grain boundary randomization on IGSCC.

2. Materials and Experimental Procedure

Two commercial grades of ASS, types 304 and 316L, were used in this study. The chemical compositions of these ASS are shown in Table 1. The grades were obtained in fully recrystallized, mill annealed state,[1] generically referred to as the as received (AR) condition. These materials were cold rolled in a laboratory rolling mill by unidirectional as well as cross rolling. Reduction in thickness from 20-80%, with an interval of 20%, was done in a number of reduction passes. The samples were solution treated at 1050 °C for 1 h and water quenched, and then sensitized at 575 °C for 1 h and at 750 °C for 48 h for type 304 and type 316L, respectively. The conditions of the materials and experimental procedures for local orientation measurements, susceptibility to degree of sensitization (DOS) by the double loop-electrochemical polarization reactivation (DL-EPR) test,[1,17,18] and to IGC by the test conforming to practice B, A 262, ASTM[1,19] were given in an earlier publication.[1]

The susceptibility to IGSCC was tested in a boiling solution of acidified 25% NaCl as per G-123 ASTM.[20] The initial pH of the solution was adjusted to 1.5. The constant strain (U-Bend) specimens were prepared following the specifications in G–30, ASTM.[21] The samples were taken out of the solution every 24 h and inspected with a magnification of 15× for presence of cracks. Samples that did not show cracks were put back in the boiling solution for further exposure. This test was carried out for the solution annealed and all the sensitized samples of type 304 and type 316L stainless steel. After the test, all the samples were examined by optical microscopy and scanning electron microscopy (SEM).

3. Results

3.1 Random Boundary Concentration and Degree of Sensitization and Intergranular Corrosion

As detailed in the earlier study,[1] with increasing reduction an increase in random boundary concentration was observed in

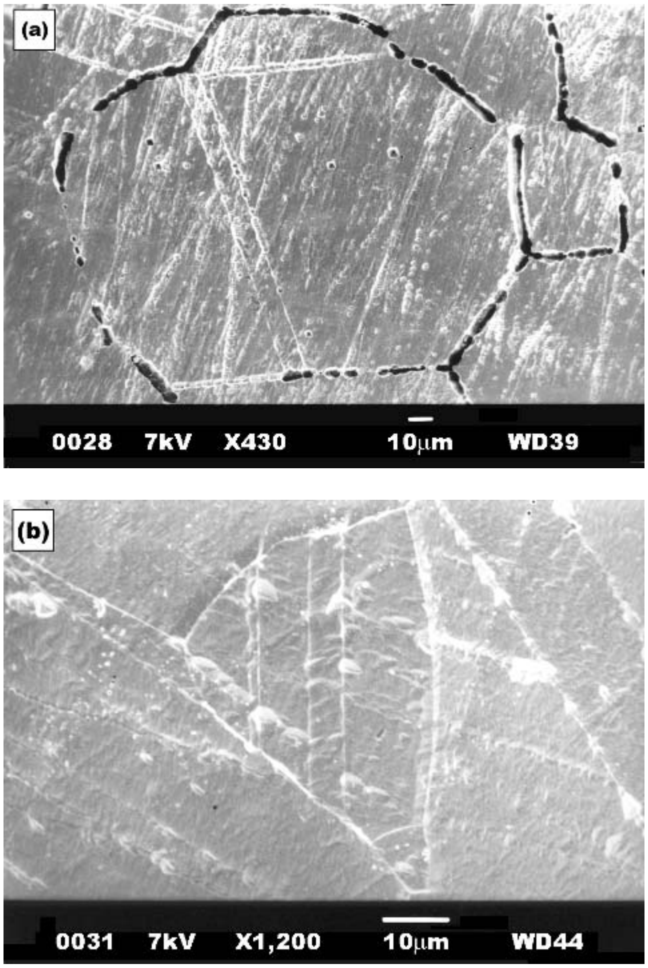

Fig. 2 SEM micrographs after the DL-EPR test showing: **(a)** attack on grain boundaries at 60% unidirectional; **(b)** no attack on grain boundaries at high percentage of reduction (i.e., 80% unidirectional rolled, where grain boundary energy is high)

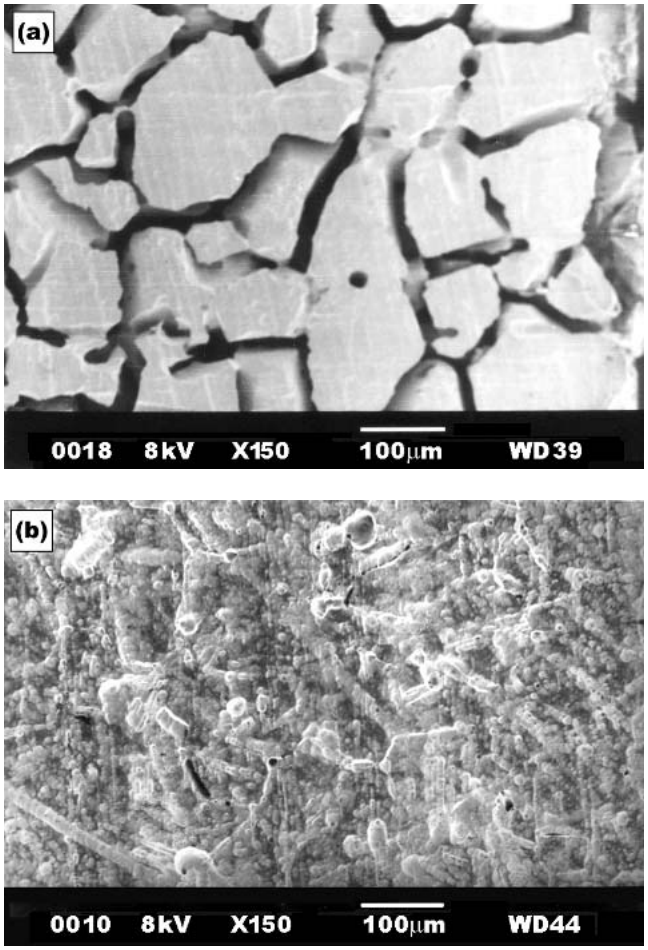

Fig. 3 SEM micrographs after ASTM A-262, practice-B, (ferric sulfate-sulfuric acid test) showing: **(a)** deep attack on grain boundaries at 60% unidirectional, **(b)** very light attack on grain boundaries and edges at high percentage of reduction (i.e., 80% unidirectional rolled, where grain boundary energy is high)

both types 304 and 316L — from about 30-40% in the AR condition to about 70-80% after 80% cold rolling (followed by solutionizing). The concentration of random boundaries is the percentage of the total length of the grain boundaries that is random ($\Sigma > 29$) out of the total length of grain boundaries (Σ 3-29 and $\Sigma > 29$) in a given sample and is measured from OIM.[1] The DOS as estimated by DL-EPR after respective sensitization treatments[1] showed an unexpected[8-11] but consistent behavior. As shown in Fig. 1 for type 304 ASS, it increased with increasing random boundary concentration, but dropped significantly beyond a "critical" value irrespective of the type of rolling (e.g., unidirectional or cross rolling). Similar behavior was also observed in type 316L ASS.[1] These results show a significant decrease in the DOS at high percentage of reduction and correspondingly high randomization of grain boundaries. Also, the IGC rates, as measured in the practice B, A262, ASTM test in type 304 ASS, were low for the 80% cold rolled, annealed, and sensitized sample.[1] These rates were comparable with those for the annealed samples.[1] The other samples with 20-60% cold working, annealing, and sensitization had shown much higher corrosion rates. The optical microscopic examination of the DL-EPR tested samples and the SEM examination of the samples tested by DL-EPR and the samples tested as per practice B, A 262, ASTM confirmed this observation. It showed considerable resistance to sensitization for materials with very high concentration of random boundaries. Figure 2(b) shows that high percentage of reduction (80% reduction with correspondingly very high concentration of random boundaries) did not result in any attack at the grain boundaries after the DL-EPR test. The attack after the DL-EPR test was clearly observed at the grain boundaries in samples with intermediate concentration of random boundaries (Fig. 2a). Figure 3(a) shows deep attack at the grain boundaries for a sample with intermediate concentration of random boundaries (60% cold worked, annealed, and sensitized sample) after the practice B, A262, ASTM test. The 80% cold worked, annealed, and sensitized sample, with very high concentration of random boundaries, did not show any attack along the grain boundaries after the practice B, A262, ASTM test (Fig. 3b). All of these results substantiate a single pattern—*significant resistance to DOS and IGC through very high concentration of random boundaries.*

Table 2 Results of the Intergranular Stress Corrosion Cracking Test in Boiling and Acidified 25% NaCl Solution (G 123, ASTM) and the Fraction of Random Grain Boundaries[1]

Material and Condition	Fraction* of Random Boundaries[1]	Duration of Testing, h	Type of Crack
Type 304 SS			
Annealed	0.32	144	TG
20% reduction + annealed + sensitized	0.46	144	IG
40% reduction + annealed + sensitized	0.51	144	IG
60% reduction + annealed + sensitized	0.72	144	IG
80% reduction + annealed + sensitized	0.77	144	TG
Type 316L SS			
Annealed	0.44	200	No Cracking
20% reduction + annealed + sensitized	0.52	200	No Cracking
40% reduction + annealed + sensitized	0.54	200	No Cracking
60% reduction + annealed + sensitized	0.55	200	No Cracking
80% reduction + annealed + sensitized	0.62	200	No Cracking

Note: The above results are for unidirectionally rolled samples only.
* Fraction of Random Boundaries = Percent Random Boundaries/100

3.2 Random Boundary Concentration and Intergranular Stress Corrosion Cracking

All of the samples of type 304 stainless steel showed cracks in the G-123 ASTM test after 144 h. However, type 316L samples did not show any cracking even when tested for 200 h. The mode of cracking (determined by optical microscopy) was transgranular in the annealed and the 80% cold rolled, annealed, and sensitized sample of type 304. The results from the G–123, ASTM test and the percentage of random boundaries (measured in an earlier study[1] by OIM) are listed in Table 2.

The optical micrographs of some typical cracks are shown in Fig. 4. The initiation of the crack was intergranular (Fig. 4a), and it subsequently changed to a mixed type (inter/transgranular) (Fig. 4b). No intergranular cracks were observed in samples with a high percentage of reduction (i.e., 80%), having a very high fraction of random grain boundaries (Fig. 4c).

4. Discussion

4.1 The Phenomenon

An increase in solutionized random boundary concentration was reported[1] in both types 304 and 316L ASS with increasing pre-solutionizing reduction percentage. Other researchers reported similar behavior.[5,6] This can be explained from the expected/observed recrystallization behavior[1,22,23]—at lower reductions recrystallization was dominated by twins, while at higher reductions it was dominated by strain localizations. The trends of DOS and IGC also followed an expected[1,8-11] trend until an intermediate or “critical” concentration of random boundaries. An unexpected and unique observation was that beyond this “critical” concentration a significant drop in DOS and IGC was observed at a very high concentration of random boundaries (Fig. 1-3 and Ref. 1.) A similar but much more subdued[2] trend was also found by other researchers when the fraction of twin boundaries was raised.[5,6]

The results of the G 123, ASTM test, to assess the susceptibility to IGSCC, showed two clear trends. First, the type 304 ASS is more prone to SCC in environments containing chloride ions compared with type 316L, in all the heat treated conditions. It may be noted that type 316L samples were tested for a longer time (200 h), whereas type 304 ASS samples showed cracking much earlier at 144 h. The higher resistance of the molybdenum containing type 316L ASS in hot environments containing chloride ions is expected.[24,25] Second, the 80% cold rolled, annealed and sensitized sample of type 304 ASS did not show IGSCC indicating high resistance to this type of localized corrosion. However, the 20-60% cold rolled samples of type 304 ASS in their annealed and sensitized condition did show IGSCC (Fig. 4). These results clearly show (Table 2) that samples with a very high fraction of random boundaries have high resistance to IGSCC. This is also indicated by the results of the DL-EPR and IGC tests (Fig. 1),[1] which showed that such samples are resistant to sensitization and IGC. Any ASS that is not sensitized would be resistant to IGSCC in environments containing chloride ions provided it is free from segregation at grain boundaries.[24] Annealed and non-sensitized ASS can be prone to transgranular SCC in these environments when the strain and/or the levels of chloride ions are high. Table 2 and Fig. 4 summarize the experimental observations of the IGSCC tests and show that when the fraction of random boundaries is increased in ASS, its resistance to IGSCC improves. The following section tries to outline a logical explanation for these results.

4.2 Possible Explanation

While it is generally accepted that the special grain boundaries (or the CSL boundaries) have low energy, therefore the probability of nucleation of precipitates is low. However, the random boundaries, with high energy, have higher probability of nucleation of precipitates. The diffusion rates of elements like chromium are very high along the random boundaries compared with those along CSL boundaries or through the grain matrix. Also, random boundaries would have numerous precipitates and thus small depletion regions adjacent to them.

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[2] As the maximum reduction was limited to about 60%.

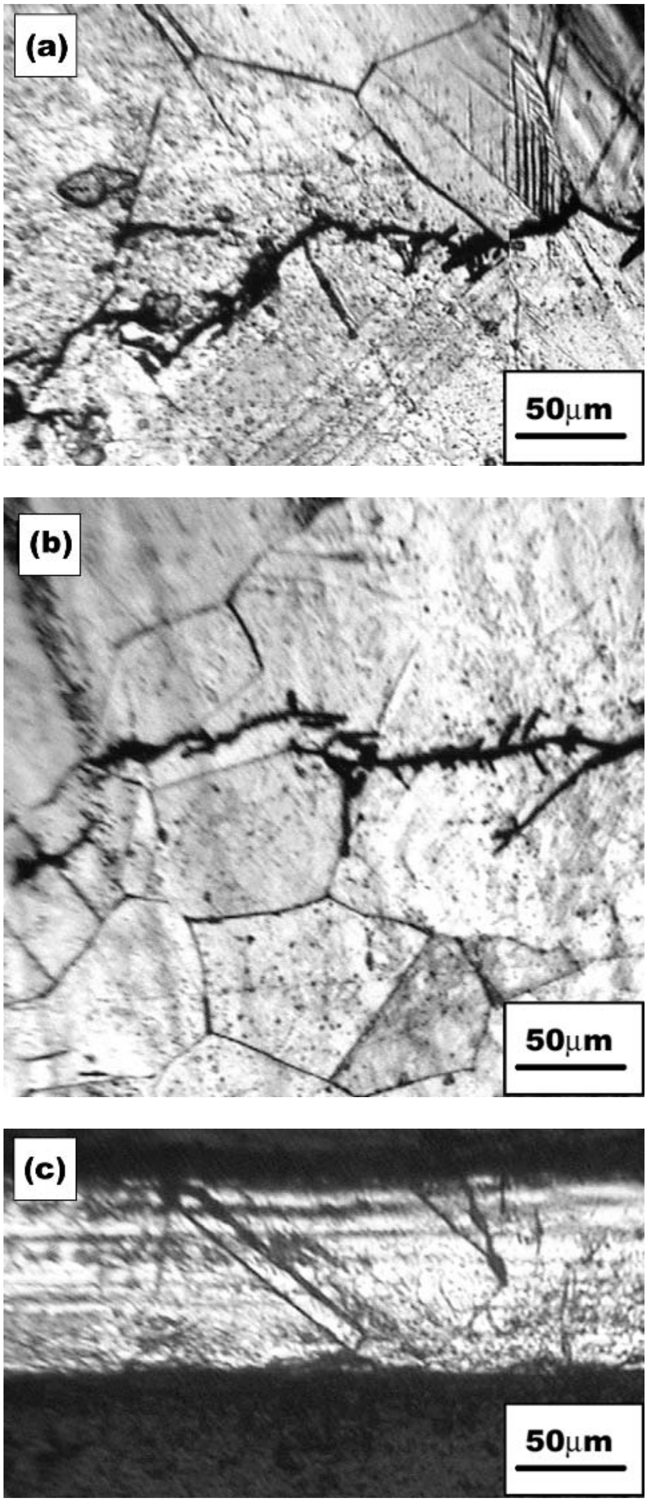

Fig. 4 Optical micrographs of cross-sectional surfaces of type 304 SS tested as per G 123, ASTM, showing typical **(a)** initiation as intergranular crack, **(b)** propagation as a mixed mode (intergranular and transgranular) crack for samples with lower percentage of reduction, annealing, and sensitization, when the fraction of random boundaries is lower (0.46-0.72), and **(c)** no cracks in most regions of the sample with high percentage (80%) of reduction in thickness, annealing, and sensitization, where the fraction of random grain boundaries is high (0.77)

A high fraction of random boundaries allows interconnectivity of grain boundaries by random boundaries. No experimental evidence is available to support this view, but high diffusion rates of chromium along interconnected random boundaries can erase the chromium depletion regions adjacent to the precipitates. Certainly the results from Ref. 1 and the current study open a new field of investigation along these lines.

5. Conclusion

A very high concentration of random boundaries offers an effective means of improving resistance to both IGC and IGSCC in austenitic stainless steels. This is mainly due to the fact that such a material is highly resistant to sensitization. While the mechanistic understanding is still to be demonstrated, the basic experimental observation of improved resistance to sensitization, IGC and IGSCC through grain boundary randomization, offers an alternate strategy to the usual thinking in grain boundary engineering and its effects on corrosion behavior.

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References

1. D. Wasnik, V. Kain, I. Samajdar, B. Verlinden, and P.K. De: “Resistance to Sensitization and Intergranular Corrosion Through Extreme Randomization of Grain Boundaries,” *Acta Mater.*, 2002, *50*(18), pp. 4587-601.
2. A.J. Sedriks: *Corrosion of Stainless Steels,* 2nd ed., John Wiley and Sons, New York, NY, 1996, p. 13.
3. H.E. Hanninen: “Influence of Metallurgical Variables on Environment-Sensitive Cracking of Austenitic Alloys,” *Int. Met. Rev.,* 1979, *3,* pp. 85-136.
4. V. Kain, R.C. Prasad, and P.K. De: “Testing Sensitization and Predicting Susceptibility to Intergranular Corrosion and Intergranular Stress Corrosion Cracking,” *Corrosion*, 2002, *59,* pp. 15-38.
5. V. Cihal: “Intergranular Corrosion of Steel and Alloys” in *Mater. Sci. Monogr.*, *18,* Elsevier, New York, NY, 1984.
6. H. Kokawa, M. Shimada, and Y.S. Sato: “Grain Boundary Structure and Precipitation in Sensitized Austenitic Stainless Steels,” *JOM*, 2000, *52*(7), pp. 34-37.
7. M. Shimada, H. Kokawa, Z.J. Wang, Y.S. Sato, and I. Karibe: “Optimization of Grain Boundary Character Distribution for Intergranular Corrosion Resistant 304 Stainless Steel by Twin Induced Grain Boundary Engineering,” *Acta Mater.,* 2002, *50*(9), pp. 2331-41.
8. T. Watanabe: “Grain Boundary Architecture for High Performance Materials” in *Boundaries and Interfaces in Materials,* The David A. Smith Symposium, R.C. Pond, W.A.T. Clark, A.H. King, and D.B. Williams, ed., The Minerals, Metals and Materials Society, Warrendale, PA, 1998, pp. 19-28.
9. P. Lin, G. Palumbo, U. Erb, and K.T. Aust: “Influence of Grain Boundary Character Distribution on Sensitization and Intergranular Corrosion of Alloy 600,” *Scripta Met. Mater.*, 1995, *33*(9), pp. 1387-92.
10. G. Palumbo: “Thermomechanical Processing of Metallic Materials,” US Patent No. 5 702 543, 1997.
11. G. Palumbo: “Metal Alloys Having Improved Resistance to Inter-

granular Stress Corrosion Cracking," US Patent No. 5 817 193, 1998.

12. D.G. Brandon: "The Structure of High Angle Grain Boundaries," *Acta Metall.*, 1966, *14,* pp. 1479-84.
13. D.A. Smith and R.C. Pond: "Bollmann's O-Lattice Theory: A Geometrical Approach to Interface Structure," *Int. Met. Rev.*, 1976, *21,* pp. 61-74.
14. A.N. Aleshin, V. Yu. Aristov, B.S. Bokshtein, and L.S. Shvindlerman: "Kinetic Properties of <111> Tilt Boundaries in Aluminum," *Phys. Stat. Sol. (A),* 1978, *45,* pp. 359-66.
15. V. Randle: *The Role of Coincident Site Lattice in Grain Boundary Engineering*, The Institute of Materials, London, UK, 1996.
16. L.E. Murr: *Interfacial Phenomena in Metal and Alloys*, Addison Wesley Publishing Co., Reading, MA, 1975; reprinted by Teck Books, Fairfax, VA, 1991.
17. A.P. Majidi and M.A. Streicher: "The Double Loop Reactivation Method for Detecting Sensitization in AISI 304 Stainless Steel," *Corrosion*, 1984, *40*(11), pp. 584-93.
18. M.A. Gaudett and J.R. Scully: "Distribution of Cr Depletion Levels in Sensitized AISI 304 Stainless Steel and Its Implications Concerning Intergranular Corrosion Phenomena," *J. Electrochem. Soc.*, 1993, *140,* pp. 3425-35.
19. Anon: "ASTM Designation A-262, Practice B" in *Annual Book of ASTM Standards,* ASTM, West Conshohocken, PA, 3.01, 2000.
20. Anon: "ASTM Designation G-123" in *Annual Book of ASTM Standards,* ASTM, West Conshohocken, PA, 3.01, 2000.
21. Anon: "ASTM Designation G-30" in *Annual Book of ASTM Standards,* ASTM, West Conshohocken, PA, 3.01, 2000.
22. F.J. Humphreys and M. Hatherly: *Recrystallization and Related Annealing Phenomena*, Elsevier Science Ltd., New York, NY, 2002.
23. D.N. Wasnik: "Grain Boundary Nature and Localized Corrosion in Austenitic Stainless Steels," Ph.D. Thesis, Indian Institute of Technology Bombay, Mumbai, India (submitted 2003).
24. A. Devansenapathi and V.S. Raja: "Effect of Externally Added Molybdate on Repassivation and Stress Corrosion Cracking of Type 304 Stainless Steel in Hydrochloric Acid," *Corrosion,* 1996, *52*(4), pp. 243-49.
25. A.J. Sedriks: "Corrosion Resistance of Austenitic Fe-Cr-Ni-Mo Alloys in Marine Environments," *Int. Met. Rev.*, 1982, *27*(6), pp. 321-53.