Effects of Forging and Heat Treatment on the Stress Corrosion Behavior of 316LN Stainless Steel in High-Temperature Alkaline Solution Postprint

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Abstract

The microstructure and residual strain of as-received, forged solution-treated, and forged stress-relieved 316LN stainless steel (316LNSS) were characterized using Electron Backscatter Diffraction (EBSD) and microhardness (HV) measurement techniques. The differences in stress corrosion cracking (SCC) behavior of the three materials in 325 ℃, 3.5% NaOH solution were investigated using the U-bend stress corrosion evaluation method. The results show that the as-received 316LNSS exhibited the highest number of SCC cracks and the maximum crack propagation rate, while the forged solution-treated 316LNSS showed the lowest SCC susceptibility; the as-received and forged solution-treated 316LNSS underwent obvious intergranular stress corrosion cracking (IGSCC) in high-temperature alkaline solution, whereas the forged stress-relieved 316LNSS experienced mixed-mode SCC; the stress relief treatment cannot effectively eliminate the banded structure that may be produced during the forging process, which is detrimental to the improvement of overall SCC resistance of 316LNSS.

Full Text

Preamble

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Effects of Forging and Heat Treatments on Stress Corrosion Behavior of 316LN Stainless Steel in High Temperature Caustic Solution

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Abstract

The reactor coolant piping in third-generation AP1000 nuclear power plants is manufactured by integral forging. Therefore, investigating the effects of forging and heat treatments on the stress corrosion cracking (SCC) resistance of 316LN stainless steel (316LNSS)—the candidate material for reactor coolant piping—is of vital importance. In this work, electron backscatter diffraction (EBSD) and microhardness measurements (HV) were used to characterize the microstructure and residual strain of as-received 316LNSS, forged and solution-annealed 316LNSS, and forged and stress-relief treated 316LNSS. The average grain size was largest in the as-received material, while the forged materials showed no obvious differences in grain size after either solution annealing or stress relief treatment. The as-received 316LNSS exhibited the highest residual strain, followed by the forged and stress-relief treated material, with the solution-annealed material showing the lowest residual strain. Moreover, residual strain in the as-received 316LNSS concentrated at grain boundaries, whereas the forged and stress-relief treated 316LNSS displayed a band-like distribution of residual strain.

U-bend specimens were utilized to evaluate SCC behavior of the three materials in high-temperature caustic solution. After SCC testing, crack morphologies were examined by SEM, and macroscopic and microscopic fracture surfaces were analyzed by OM and SEM, respectively. Grain morphology, residual strain distribution, and grain boundary character near SCC crack tips in the forged and stress-relief treated 316LNSS were investigated using EBSD. The results showed that the forged and solution-annealed 316LNSS exhibited the lowest SCC sensitivity, while the as-received material showed the highest sensitivity with the most numerous cracks and highest growth rate. The as-received and forged-solution-annealed materials displayed obvious intergranular stress corrosion cracking (IGSCC), whereas the forged and stress-relief treated material showed a mixed cracking mode. The larger average grain size and higher residual strain, particularly its concentration at grain boundaries, were responsible for the highest SCC sensitivity of the as-received material. Compared with the stress-relief treated material, the higher content of coincidence site lattice boundaries (CSLB) and lower residual strain contributed to the superior SCC resistance of the solution-annealed material. Stress-relief treatment failed to effectively eliminate the band-like microstructure formed during forging, which was detrimental to overall SCC resistance.

Keywords: stainless steel, nuclear material, stress corrosion cracking, high temperature caustic solution, fractography

Introduction

International operating experience from advanced nuclear countries demonstrates that material failures, primarily in the form of stress corrosion cracking (SCC), have become a significant cause of component failure in nuclear power plants and warrant sufficient attention. Extensive research has been conducted on SCC behavior of nuclear structural materials in high-temperature, high-pressure water environments. These studies indicate that crack initiation and growth rates are influenced by irradiation, stress level, water chemistry parameters (temperature, pH, dissolved oxygen, and dissolved hydrogen), yield strength, and microstructure. Zhang and Wang employed the direct current potential drop (DCPD) method to monitor SCC crack growth rates (CGR) of 316L stainless steel (316LSS) in simulated pressurized water reactor environments, finding that CGR increased with dissolved oxygen content and exhibited pronounced intergranular SCC (IGSCC) characteristics. Lu et al. reported that one-dimensionally hot-rolled 304L stainless steel showed different CGR values along different sampling directions in high-temperature water, attributing this to microstructural anisotropy and loading direction.

Stainless steels exhibit high SCC susceptibility in high-temperature alkaline solutions, making this an effective method for rapidly evaluating service reliability under extreme conditions and providing important guidance for material selection in nuclear applications. Yang et al. compared SCC behavior of Alloys 690 and 800—materials used for steam generators—in boiling 50% NaOH solution, finding that the higher chromium content in the oxide film on Alloy 690 improved its protectiveness and reduced SCC susceptibility.

The primary coolant piping in China’ s under-construction third-generation AP1000 nuclear plants uses integrally forged 316LN stainless steel (316LNSS). However, most existing research has focused on SCC behavior of cast or cold-worked stainless steels and nickel-based alloys, with relatively few studies on forged stainless steel in high-temperature water. This work analyzes the influence of forging and heat treatment processes on SCC susceptibility of 316LNSS in high-temperature alkaline solution, providing data support for optimizing the manufacturing process of large, thick-walled primary coolant piping in China.

1 Experimental Methods

The material used was 316LNSS for nuclear power plant primary coolant piping, with chemical composition (mass fraction, %) of: C 0.010, Cr 17.07, Ni 12.87, Mn 1.35, S 0.003, P 0.023, N 0.12, Si 0.26, Cu 0.06, Mo 2.21, Fe balance. The material was first subjected to multi-directional forging with a forging ratio of 7, followed by either solution treatment or stress-relief treatment. Details of the forging and heat treatment procedures are provided in reference [11], yielding three material conditions: as-received (S0), forged and solution-annealed (S71), and forged and stress-relief treated (S72). The room-temperature mechanical properties of the three materials are listed in Table 1 .

Specimens measuring 10 mm × 10 mm × 2 mm were cut by wire electrical discharge machining. Sample surfaces were ground sequentially with metallographic abrasive paper to 2000 grit, then mechanically polished with diamond paste to 2.5 m. Some specimens were electrolytically etched in 10% oxalic acid solution (mass fraction) for examination of grain boundaries and inclusions using an XL30FEG scanning electron microscope (SEM). Other specimens were tested for surface micro-Vickers hardness using an MHVD-1000AP digital microhardness tester with a load of 200 g and dwell time of 15 s; ten measurements were taken on each sample with 1 mm spacing. Electron backscatter diffraction (EBSD) was employed to characterize grain boundary structure and residual strain distribution. EBSD scans were performed on the XL30FEG SEM, with sample preparation and data analysis described in reference [11]. The EBSD results for S0 were previously reported in [11] but are included here for comparative purposes.

U-bend specimens were prepared according to ASTM G30 standard with dimensions of 50 mm × 15 mm × 2 mm, as shown in Figure 1 [Figure 1: see original paper]. All six surfaces of the plate specimens were ground with waterproof abrasive paper to 400 grit to achieve a surface roughness of 0.14 m < Ra < 0.20 m. The specimens were then U-bent using an SFL-5-350 fatigue testing machine and fastened with 316L stainless steel bolts while maintaining parallel arms. Three parallel specimens were prepared for each material condition. Prior to testing, specimens were examined under a Leica S6D stereomicroscope (OM) for surface defects, ultrasonically cleaned in an acetone-ethanol solution, and dried.

Immersion testing of U-bend specimens was conducted in a static autoclave with a pure Ni liner. The test solution was 3.5% NaOH by mass, prepared using analytical-grade NaOH and deionized water. The solution was deoxygenated with high-purity N for 4 h at 70 °C before heating. The temperature was then raised to 325 °C and held for 52 h. Heating required approximately 5 h, and cooling from 325 °C to room temperature required about 12 h.

After immersion testing, some specimens were soaked in liquid nitrogen for approximately 1.5 h and then fractured along the crack propagation direction for examination of macroscopic fracture morphology by OM and microscopic fracture morphology and crack propagation paths by SEM. To investigate the relationship between crack propagation path and grain boundary structure/residual strain distribution, EBSD scans were performed on the U-bend specimen of S72 material. The cracked S72 specimen was prepared by grinding the cross-section to 2000 grit, mechanically polishing with diamond paste to 1.5 m, and finally manually polishing for 3 h with 0.02 m SiO suspension to remove the surface strain layer. The EBSD scan step size was 2 m, with data acquisition and analysis described in reference [11].

2 Results

2.1 Microstructure and Residual Strain

Figure 2 [Figure 2: see original paper] shows EBSD images of the three 316LNSS specimens. All three materials contained numerous twins with non-uniform grain sizes. Statistical analysis revealed average grain sizes of 463.6 m, 157.2 m, and 191.1 m for S0, S71, and S72, respectively. The forged 316LNSS did not exhibit coarse original grains, indicating complete recrystallization. As a single-phase austenitic stainless steel, 316LNSS does not undergo phase transformation during heating and cooling; therefore, forging refined the grain size, while subsequent heat treatment had no significant effect on grain size.

Figure 3 [Figure 3: see original paper] presents SEM images of inclusions in the three specimens. The materials contained very few inclusions, approximately 3 m in size, distributed both within grains and at grain boundaries. EDS analysis (not shown) indicated that most inclusions were Al-containing oxides, with some containing Ca, Mg, and Nb elements.

Figure 4 [Figure 4: see original paper] shows the room-temperature microhardness of the three 316LNSS specimens, following the trend S0 > S72 > S71. Carlsson and Larsson confirmed that microhardness correlates well with strain hardening but not precisely with residual stress. Therefore, the hardness measurements indicate that S0 had the highest residual strain level, S72 had intermediate strain, and S71 had the lowest residual strain.

Kernel average misorientation (KAM) maps quantitatively characterize microscale strain. The KAM maps for the three 316LNSS specimens are shown in Figure 5 [Figure 5: see original paper]. The average KAM values were 1.01, 0.46, and 0.91 for S0, S71, and S72, respectively, confirming that S0 contained the highest residual strain while S71 contained the lowest. Notably, the distribution of residual strain differed significantly among the specimens: S0 showed strain concentrated near grain boundaries, whereas S71 and S72 exhibited strain distributed within grains. For S72 in particular, the residual strain distribution was highly heterogeneous, with highly strained grains connected in a "band-like" pattern.

Figure 6 [Figure 6: see original paper] displays grain boundary character maps for the three 316LNSS specimens. Green lines represent low-angle boundaries

(LAB), red lines represent coincidence site lattice boundaries (CSLB), and blue lines represent random high-angle boundaries (RGB). The background grayscale indicates grain average image quality (GAIQ). The grain boundary character distribution (GBCD) is quantified in Table 2 . Regions with dense LAB distributions appear darker, indicating higher microstrain. Compared with S72, S71 exhibited higher CSLB content and lower LAB content, with similar RGB content. The boundaries corresponding to the "band-like" structure in Figure 5b were primarily RGB with numerous LAB. Since LAB consist of arrays of dislocations, regions with high LAB content have higher dislocation densities and greater microstrain.

Forging and heat treatment affected the recrystallization behavior of 316LNSS during thermomechanical processing, thereby significantly influencing grain size, residual strain level and distribution, and grain boundary characteristics. Detailed analysis is provided in reference [11].

2.2 SCC Susceptibility

Figure 7 [Figure 7: see original paper] shows cross-sectional SEM images of the U-bend specimens after SCC testing. SCC cracks in all three materials initiated and propagated preferentially at the outer surface apex. Lu et al. confirmed using X-ray diffraction that the apex of U-bend specimens experiences high residual tensile stresses, representing the location of highest SCC susceptibility. The main crack in each specimen had nearly penetrated the entire thickness, though the main crack in S0 was notably coarser and more easily observed. The number and length of SCC cracks reflect SCC susceptibility. In addition to the central crack, S0 and S72 specimens also cracked at other locations, indicating higher SCC susceptibility.

Figure 8 [Figure 8: see original paper] shows crack morphologies at the apex of U-bend specimens after SCC testing. S0 exhibited the most severe cracking with multiple initiation sites, indicating the highest SCC susceptibility. Cracks in S71 initiated and propagated primarily at the apex of the U-bend specimen. In S72, cracks were distributed diagonally, suggesting varying SCC susceptibility at different positions along the apex and different crack initiation times and growth rates.

Macroscopic fracture morphologies of the main cracks in the three U-bend specimens are shown in Figure 9 [Figure 9: see original paper]. Regions manually fractured in air after removal from the autoclave appear bright, while areas where SCC crack propagation occurred in the high-temperature alkaline solution appear dark. The 316LNSS exhibited high SCC susceptibility in the high-temperature NaOH solution, with severe SCC observed after 52 h of immersion. The average SCC crack lengths through the specimen thickness followed the order: S0 > S72 > S71. Cracks in S0 and S71 were relatively straight, whereas S72 showed significant variation in crack length, indicating that different locations in S72 had substantially different crack initiation and growth rates, unlike

S0 and S71 where these rates were more uniform.

Figure 10 [Figure 10: see original paper] shows fracture surface morphologies of the main cracks in the three U-bend specimens. The grain size in S0 was significantly larger than in S71 and S72, consistent with the EBSD results. S0 and S71 exhibited clear intergranular brittle fracture with a rock-candy morphology, while S72 showed a mixed fracture mode with both transgranular (cleavage) and intergranular features. This fracture morphology is similar to that observed for Alloy 690 in acidic NaCl solution. According to the Cr-H O potential-pH diagram at 300 °C and other studies, chromium may exist as CrO ^{2} in strongly alkaline conditions, placing it in a thermodynamically unstable state and resulting in non-protective oxide films. Therefore, 316LNSS undergoes active dissolution in high-temperature NaOH solution, and the SCC mechanism is anodic dissolution-controlled.

Figure 11 [Figure 11: see original paper] presents EBSD images near the crack tip and surrounding region in the S72 specimen. Due to severe plastic deformation during U-bend specimen preparation, the EBSD image of the cracked S72 specimen differs significantly from Figures 5 and 6. The cross-section shows intergranular SCC (IGSCC), with RGB being the preferred crack propagation path and some SCC cracks arrested at CSLB. SCC cracks propagated along regions with high residual microstrain. S72 exhibited mixed-mode SCC, with some grains showing IGSCC and others showing transgranular SCC (TGSCC). The EBSD image in Figure 11 reflects the IGSCC propagation path in this particular cross-section.

3 Analysis and Discussion

Metallic SCC behavior results from the combined effects of environmental, mechanical, and material factors. Key material factors affecting SCC susceptibility include yield strength, grain size, grain boundary structure, grain boundary chemistry and carbides, and residual stress/strain distribution. Since the 316LNSS used in this work contained very few inclusions and grain boundary precipitates (Figure 3) of small size, the analysis focuses on how yield strength, residual strain, grain size, and grain boundary characteristics influence SCC behavior.

3.1 Effect of Yield Strength on SCC Behavior

Yield strength characterizes macroscopic mechanical properties, and materials with different yield strengths typically exhibit different SCC susceptibilities. For the three 316LN specimens, higher yield strength (Rp .) correlated with longer SCC cracks and thus higher SCC susceptibility, consistent with the trend of increasing CGR with yield strength in stainless steels in high-temperature water. From an engineering perspective, forging and heat treatment altered the yield strength of 316LNSS, thereby causing differences in SCC susceptibility. Shoji et al. proposed that higher yield strength materials have larger strain gradients and smaller plastic zones at crack tips, affecting SCC growth rates. Although the mechanism by which yield strength influences SCC is not fully understood, Terachi et al. provided an empirical formula showing CGR is proportional to yield strength for stainless steels in high-temperature water. For nuclear structural materials, irradiation and cold working increase yield strength, which is closely related to microstructure; therefore, analysis of SCC susceptibility should focus on microstructural and microstrain effects of forging and heat treatment.

3.2 Effect of Residual Strain on SCC Behavior

Hou et al. demonstrated that strain concentration at grain boundaries in cold-worked Alloy 600 is an important factor increasing SCC susceptibility in high-temperature water. Stainless steels with different cold-work levels exhibit different residual strain levels and correspondingly different CGR values. The 316LNSS undergoes active dissolution in high-temperature NaOH solution (Figure 10), and higher residual strain may accelerate active dissolution, thereby promoting SCC initiation and propagation. Figure 11 also shows that SCC in S72 preferentially propagated along regions with high residual strain. The distinct residual strain distributions in S0 versus S71 and S72 (Figure 5), combined with fracture morphologies (Figure 10), demonstrate that residual strain significantly affects both SCC growth rate and propagation path. Strain concentration near grain boundaries in S0 promoted IGSCC and multiple cracking sites (Figures 7 and 8). S71 exhibited IGSCC but had minimal residual strain and less grain boundary strain concentration, resulting in the slowest crack growth rate. In S72, cracks propagated both along grain boundaries and through grain interiors, likely because high residual strain in some grains enhanced active dissolution, leading to mixed-mode SCC. Overall, S72' s residual strain level was intermediate between S0 and S71, and its crack growth rate was correspondingly intermediate. The non-uniform crack length distribution in S72 (Figure 9) may be related to the heterogeneous distribution of residual strain (Figure 5c). For thermomechanically processed materials, large residual strain gradients between adjacent grains with significantly different strain levels become preferential sites for SCC propagation. In summary, grain boundary strain concentration increased SCC susceptibility of as-received 316LNSS, while forging and subsequent heat treatment improved SCC resistance by altering this strain distribution. Compared with stress-relief treatment, solution annealing after forging more effectively reduced residual strain and eliminated its heterogeneous distribution, thereby improving overall SCC resistance.

3.3 Effect of Grain Size and Boundary Structure on SCC

Different grain sizes mean different grain boundary area fractions and different numbers of triple junctions. SCC cracks typically initiate at triple junctions and propagate directly to the next triple junction, where they may be arrested. Further propagation requires repeated re-initiation at triple junctions; thus, more triple junctions create greater resistance to crack growth. The average grain size of S0 was significantly larger than that of S71 and S72 (Figure 2), which may partly explain why SCC cracks in S0 were substantially longer than in S71 and S72. The grain sizes of S71 and S72 were similar, so differences in their SCC susceptibility likely arose from other factors such as yield strength, residual strain level, and grain boundary structure.

When grain sizes are similar, differences in grain boundary structure become important. Grain boundaries were classified as LAB, CSLB, or RGB. CSLB are "special boundaries" —ordered, low-energy boundaries with excellent SCC resistance. Alexandreanu and Was proposed that IGSCC behavior of Ni-16Cr-9Fe alloy in high-temperature water correlates with grain boundary deformation capability, with CSLB being more resistant to deformation and thus more SCC-resistant. S71 had significantly higher CSLB content than S72 (Table 2), resulting in lower average SCC crack growth rates. The mixed-mode SCC in S72 was related not only to residual strain but also to the high LAB content within some grains (Table 2 and Figure 6), which provided favorable sites for transgranular cracking after crack initiation at grain boundaries. Additionally, S72 exhibited greater grain size heterogeneity, with the band-like structure corresponding to larger grains (Figure 5b) that were primarily bounded by RGB. This band-like structure, characterized by high residual strain, large grain size, and RGB character, was detrimental to SCC resistance. Therefore, based on these results, solution annealing after forging is recommended in actual production to eliminate the band-like microstructure that may form during forging.

4 Conclusions

(1) 316LN stainless steel undergoes active dissolution in high-temperature alkaline solution with high SCC susceptibility, exhibiting obvious stress corrosion cracking after 52 h of immersion. Forging and heat treatment affect SCC behavior by altering yield strength, residual strain, grain size, and grain boundary structure.

(2) As-received and forged-solution-annealed 316LNSS exhibited clear intergranular SCC in high-temperature alkaline solution, while forged and stress-relief treated 316LNSS showed mixed-mode SCC, primarily due to high residual strain in local grains and high LAB content.

(3) In as-received 316LNSS, residual strain concentrated near grain boundaries, whereas forging and heat treatment dispersed residual strain within grains, demonstrating that thermomechanical processing can reduce residual strain and improve its distribution, thereby suppressing crack initiation and propagation. However, stress-relief treatment could not eliminate the band-like structure formed during forging, which featured high residual strain, large grain size, and primarily random high-angle boundaries. This was detrimental to overall SCC resistance. Therefore, solution treatment is recommended after forging of primary coolant piping.

References

[1] Han E-H. Acta Metall Sin, 2011; 47: 769
[2] Zinkle S J, Was G S. Acta Mater, 2013; 61: 735
[3] Andresen P L, Morra M M. J Nucl Mater, 2008; 383: 97
[4] Zhang L, Wang J Q. J Nucl Mater, 2014; 446: 15
[5] Ma C, Peng Q J, Han E-H, Ke W. J Chin Soc Corros Prot, 2014; 34: 37
[6] Lu Z, Shoji T, Dan T, Qiu Y, Yonezawa T. Corros Sci, 2010; 52: 2017
[7] Yang W, Lu Z, Huang D, Kong D, Zhao G, Congleton J. Corros Sci, 2001; 43: 963
[8] Berge P, Donati J R, Prieux B, Villard D. Corrosion, 1977; 33: 425
[9] Meng F, Lu Z, Shoji T, Wang J Q, Han E-H, Ke W. Corros Sci, 2011; 53: 2558
[10] Lu Y H, Chen Z R, Zhu X F. J Univ Sci Technol Beijing, 2013; 35: 1320
[11] Guo Y, Han E-H, Wang J Q. J Mater Sci Technol, 2015; 31: 403
[12] Carlsson S, Larsson P L. Acta Mater, 2001; 49: 2179
[13] Lu J Z, Luo K Y, Yang D K, Cheng X N, Hu J L, Dai F Z, Qi H, Zhang L, Zhong J S, Wang Q W, Zhang Y K. Corros Sci, 2012; 60: 145
[14] Wang S, Wang J Q. Corros Sci, 2014; 85: 183
[15] Staehle R W, Gorman J A. Corrosion, 2003; 59: 931
[16] Zhang Z, Wang J Q, Han E-H, Ke W. J Mater Sci Technol, 2012; 28: 785
[17] Yu G P, Yao H C. Corrosion, 1990; 46: 391
[18] Zhang Z M, Peng Q J, Wang J Q, Han E-H, Ke W. J Chin Soc Corros Prot, accepted
[19] Zheng J H, Bogaerts W F, Brabers M J. Corrosion, 1992; 48: 320
[20] Terachi T, Yamada T, Miyamoto T, Arioka K. J Nucl Mater, 2012; 426: 59
[21] Shoji T, Li G, Kwon J, Matsushima S, Lu Z. Proceedings of the 11th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Warrendale, PA: TMS, 2003: 834
[22] Hou J, Peng Q J, Shoji T, Wang J Q, Han E-H, Ke W. Corros Sci, 2011; 53: 2956
[23] Hou J, Peng Q J, Lu Z P, Shoji T, Wang J Q, Han E-H, Ke W. Corros Sci, 2011; 53: 1137
[24] Meng F, Han E-H, Wang J Q, Zhang Z, Ke W. Electrochim Acta, 2011; 56: 1781
[25] Hu C L, Xia S, Li H, Liu T G, Zhou B X, Chen W J. Acta Metall Sin, 2011; 47: 939
[26] Alexandreanu B, Was G S. Corrosion, 2003; 59: 705

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