Effects of Forging and Heat Treatment on Stress Corrosion Behavior of 316LN Stainless Steel in High-Temperature Alkaline Solutions 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 3.5% NaOH solution at 325 °C 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 exhibited obvious intergranular stress corrosion cracking (IGSCC) in the high-temperature alkaline solution, whereas the forged stress-relieved 316LNSS underwent mixed-mode SCC; the stress relief treatment cannot effectively eliminate the banded structure that may be generated during the forging process, which is detrimental to the improvement of overall SCC resistance of 316LNSS.

Full Text

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 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 grain size differences after solution annealing or stress relief treatment. The as-received material exhibited the highest residual strain, followed by the forged and stress-relief-treated material, with the solution-annealed material showing the lowest residual strain. Notably, residual strain in the as-received material concentrated at grain boundaries, whereas the forged and stress-relief-treated material displayed a band-like residual strain distribution. U-bend specimens were utilized to evaluate SCC behavior in high-temperature caustic solution. After SCC testing, crack morphologies were examined by SEM, and macroscopic and microscopic fracture features were analyzed by optical microscopy and SEM, respectively. EBSD was employed to investigate grain morphology, residual strain, and grain boundary character distribution near SCC crack tips in the forged and stress-relief-treated material. Results showed that the forged and solution-annealed material exhibited the lowest SCC susceptibility, while the as-received material showed the highest susceptibility with the most cracks and highest growth rate. The as-received and forged-solution-annealed materials displayed obvious intergranular SCC (IGSCC), whereas the forged and stress-relief-treated material exhibited mixed-mode cracking. The larger average grain size and higher residual strain, particularly concentrated at grain boundaries, were responsible for the highest SCC susceptibility in the as-received material. Compared with the stress-relief-treated condition, the higher coincidence site lattice boundary (CSLB) content and lower residual strain contributed to lower SCC susceptibility in the solution-annealed material. Stress relief treatment failed to effectively eliminate the band-like microstructure formed during forging, which disadvantaged overall SCC resistance.

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

1. Introduction

International operating experience from advanced nuclear power 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 the SCC behavior of nuclear structural materials in high-temperature, high-pressure water environments. Results indicate that SCC crack initiation and growth rates are influenced by irradiation, stress level, water chemistry parameters (temperature, pH, dissolved oxygen, dissolved hydrogen), yield strength, and microstructure. Zhang and Wang used 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 IGSCC characteristics. Lu et al. reported that one-dimensionally hot-rolled 304L stainless steel showed different CGRs along different sampling directions in high-temperature water, attributed 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 (steam generator materials) in boiling 50% NaOH solution, finding that the higher Cr content in Alloy 690's surface oxide film improved 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 focuses 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 manufacturing processes for large, thick-walled primary loop piping.

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2. Experimental Methods

The 316LNSS used in this study had a 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 underwent multi-directional forging with a forging ratio of 7, followed by either solution treatment or stress relief treatment. Detailed forging and heat treatment procedures are described in reference [11]. Three material conditions were produced: as-received (S0), forged and solution-annealed (S71), and forged and stress-relief-treated (S72). Room-temperature mechanical properties of the three materials are shown in

Table 1 .

Samples measuring 10 mm × 10 mm × 2 mm were cut by wire electrical discharge machining. Surfaces were ground sequentially with metallographic abrasive paper to 2000 grit, then mechanically polished with diamond paste to 2.5 m. Some samples 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 samples were measured for surface micro-Vickers hardness using an MHVD-1000AP digital microhardness tester with a 200 g load and 15 s dwell time; 10 measurements were taken per sample with 1 mm spacing. EBSD was employed to characterize grain boundary structure and residual strain distribution in 316LNSS. EBSD scans were performed on the XL30FEG SEM; sample preparation and data analysis are described in reference [11]. EBSD results for S0 were previously reported in reference [11] and 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 samples were ground with wet abrasive paper to 400 grit to achieve a surface roughness of 0.14 m $<$ Ra $<$ 0.20 m. Samples 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, samples were inspected for surface defects using a Leica S6D stereomicroscope (OM) and ultrasonically cleaned in an acetone-alcohol solution before drying.

U-bend immersion tests were conducted in a static autoclave with a pure Ni liner. The test solution was 3.5% NaOH (mass fraction) prepared with analytical-grade NaOH and deionized water. The solution was deoxygenated with high-purity N_2 for 4 h at 70 °C before heating. Temperature was then increased to 325 °C and held for 52 h. Heating required approximately 5 h, and cooling from 325 °C to room temperature required approximately 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. Macroscopic fracture morphologies were examined by OM, and microscopic fracture morphologies and crack propagation paths were observed by SEM. To investigate relationships between crack propagation path, grain boundary structure, and residual strain distribution, EBSD scans were performed on U-bend specimens of S72 material. Cracked EBSD samples were prepared by grinding the cross-section to 2000 grit, mechanically polishing with diamond paste to 1.5 m, and final manual polishing for 3 h with 0.02 m SiO_2 suspension to remove the surface strain layer. EBSD scan step size was 2 m; data collection and analysis are described in reference [11].

2.1 Microstructure and Residual Strain

Figure 2 [Figure 2: see original paper] shows EBSD images of the three 316LNSS specimens. All three 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. No coarse original grains remained in the forged 316LNSS, 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 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. Inclusions were very scarce, approximately 3 m in size, and 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 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.

Kernel average misorientation (KAM) maps quantitatively characterize microscale strain. KAM maps for the three specimens are shown in Figure 5 [Figure 5: see original paper]. 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. The distribution of residual strain differed markedly among the specimens: S0 showed strain concentrated near grain boundaries, whereas S71 and S72 exhibited strain distributed within grains. For S72 in particular, residual strain distribution was highly heterogeneous, with heavily strained grains connecting to form a “band-like” structure.

Figure 6 [Figure 6: see original paper] shows grain boundary character maps for the three 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). Background grayscale indicates grain average image quality (GAIQ). Grain boundary character distribution (GBCD) is summarized 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. Grain boundaries corresponding to the “band-like” structure in Figure 5b were primarily RGB with numerous LABs. Since LABs consist of arrays of dislocations, high LAB content corresponds to high dislocation density and thus high microstrain.

Forging and heat treatment affected recrystallization behavior 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 316LNSS U-bend specimens after SCC testing. SCC cracks in all three specimens 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 most SCC-susceptible location. The primary crack in the center had nearly penetrated through the specimen thickness in all cases, though it was coarser and more easily observed in S0. The number and length of SCC cracks reflect SCC susceptibility. In addition to the central crack, S0 and S72 showed cracking 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 pronounced feature: multiple cracks at the specimen apex, indicating the highest SCC susceptibility. Cracks in S71 initiated and propagated primarily at the apex, while cracks in S72 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 primary 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 propagated in the high-temperature alkaline solution appear dark. 316LNSS exhibited high SCC susceptibility in the high-temperature NaOH solution, with severe SCC cracking after 52 h immersion. The average SCC crack length through the specimen thickness followed the order: S0 > S72 > S71. Cracks in S0 and S71 were relatively straight, while S72 showed significant length fluctuations, indicating large variations in crack initiation and growth rates at different locations, unlike the relatively uniform behavior in S0 and S71.

Figure 10 [Figure 10: see original paper] shows fracture morphologies of primary cracks in the three U-bend specimens. S0 exhibited significantly larger grain sizes than S71 and S72, consistent with EBSD results. S0 and S71 showed obvious intergranular brittle fracture with a rock-candy morphology, while S72 displayed mixed-mode cracking with both transgranular (cleavage) and intergranular features. These fracture morphologies resemble those of Alloy 690 in acidic NaCl solution. According to the Cr-H_2O potential-pH diagram at 300 °C and other studies, Cr may exist as ${CrO_4}^{2-}$ 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 S72. Due to severe plastic deformation during U-bend specimen preparation, the cracked S72 EBSD images differ significantly from those in Figures 5 and 6. The images show IGSCC in this cross-section, with RGBs being the preferred crack propagation paths and some SCC cracks terminating at CSLBs. 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 crack propagation path in one cross-section, indicating IGSCC in this region.

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3. Analysis and Discussion

SCC behavior results from the combined effects of environmental, mechanical, and material susceptibility 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. Inclusions and grain boundary precipitates were very scarce in the 316LNSS used in this work (Figure 3) and were small in size. Therefore, analysis focuses on yield strength, residual strain, grain size, and grain boundary characteristics to explain forging and heat treatment effects on SCC behavior in high-temperature alkaline solution.

3.1 Influence 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 ($\mathrm{Rp}_{0}\cdot_{2}$) corresponded to longer SCC cracks and thus higher SCC susceptibility, consistent with the trend of increasing CGR with yield strength for stainless steels in high-temperature water. From an engineering perspective, forging and heat treatment altered the yield strength of 316LNSS, thereby causing different SCC susceptibilities. Shoji et al. proposed that higher yield strength materials have larger strain gradients and smaller crack-tip plastic zones, affecting SCC growth rates. Although the mechanism by which yield strength influences SCC behavior remains unclear, 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, microstructural and microstrain perspectives are needed to analyze how forging and heat treatment affect SCC susceptibility.

3.2 Influence of Residual Strain on SCC Behavior Hou et al. demonstrated that strain concentration at grain boundaries in cold-worked Alloy 600 is an important cause of increased SCC susceptibility in high-temperature water. Stainless steels with different cold-work levels exhibit different residual strain levels and correspondingly different CGRs. 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), indicate that residual strain significantly affects both SCC growth rate and propagation path. Obvious strain concentration near grain boundaries in S0 promoted IGSCC and multiple cracking sites (Figures 7 and 8). S71 exhibited IGSCC but had the lowest residual strain and less grain boundary strain concentration, resulting in the slowest crack growth rate. In S72, cracks propagated both along grain boundaries and within grains, likely because high residual strain in some grains accelerated active dissolution, leading to mixed-mode SCC. Overall, S72's residual strain level was intermediate between S0 and S71, and its SCC crack growth rate was also intermediate. Additionally, the non-uniform crack lengths in S72 (Figure 9) may be related to the heterogeneous residual strain distribution (Figure 5c). Based on Figure 11, for forged and heat-treated materials, large residual strain gradients between adjacent grains with significantly different strain levels become preferred sites for SCC propagation. In summary, grain boundary strain concentration increased SCC susceptibility in 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 Influence 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 were longer in S0. S71 and S72 had similar grain sizes, so differences in 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. CSLBs are "special boundaries"—ordered, low-energy boundaries with excellent SCC resistance. Additionally, Alexandreanu and Was proposed that IGSCC behavior of Ni-16Cr-9Fe alloy in high-temperature water correlates with grain boundary deformation capability, with CSLBs being more resistant to deformation and thus more SCC-resistant. Compared with S72, S71 had significantly higher CSLB content (Table 2) and thus lower average SCC crack growth rate. The most distinctive feature of S72—mixed-mode SCC—is directly related to residual strain and may also be attributed to high LAB content within some grains (Table 2 and Figure 6), which provides favorable sites for transgranular cracking after crack initiation at grain boundaries.

Furthermore, S72 had greater grain size heterogeneity, and grains corresponding to the band-like structure in Figure 5b were also relatively large. Thus, the band-like structure in S72 not only had high residual strain but also large grain sizes with primarily RGB character, reducing SCC resistance. Based on these results, solution treatment after forging is recommended in actual production to eliminate band-like structures that may form during forging.

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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 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 obvious intergranular SCC in high-temperature alkaline solution, while forged and stress-relief-treated 316LNSS showed mixed-mode SCC, primarily caused by high residual strain in local grains and high LAB content.
3. In as-received 316LNSS, residual strain concentrated near grain boundaries, while in forged and heat-treated materials, residual strain was distributed within grains. Forging and subsequent heat treatment reduced residual strain and improved its distribution, thereby suppressing crack initiation and propagation. However, stress relief treatment could not eliminate band-like structures formed during forging. The band-like structure, characterized by high residual strain, large grain size, and primarily RGB character, is detrimental to overall SCC resistance. Therefore, solution treatment is recommended after forging of primary coolant piping.

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