Postprint: Study on Properties of Warm-Rolled High-Aluminum 304 Austenitic Stainless Steel

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Abstract

Warm rolling and solution treatment were performed on high-aluminum 304 austenitic stainless steel. The surface morphology, phase composition, and surface composition of the alloy were analyzed using optical microscopy (OM), X-ray diffraction (XRD), and electron probe microanalysis (EPMA), respectively, and its mechanical properties were tested and analyzed. The results show that in the microstructure of the high-aluminum alloy, the black ferrite phase appears as strip-like, short rod-like, and partially granular forms distributed on the white austenite matrix, with a directional microstructure distribution; most of the Al element is dissolved in the matrix, accompanied by the precipitation of black phases such as AlN; with increasing rolling temperature, the hardness and corrosion resistance gradually increase, and the elongation reaches approximately 47%; the deformability of the high-aluminum alloy is significantly improved, and the tensile strength of the 1%Al (mass fraction, hereinafter the same) alloy can reach 766 MPa; the fracture surfaces of the alloys are composed of large dimples (5-15 m) and small dimples (5 m), and the fracture modes of the alloys at different rolling temperatures are similar, all belonging to ductile fracture; under the same rolling temperature, the 1.5%Al stainless steel exhibits better corrosion resistance.

Full Text

Properties of Warm-Rolled High-Aluminum 304 Austenitic Stainless Steel

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Abstract
304 stainless steels with different aluminum contents were warm-rolled and subsequently solution-treated. The microstructure, phase constituents, and composition of the alloys were characterized by optical microscopy (OM), X-ray diffraction (XRD), and electron probe microanalysis (EPMA). The results show that the black ferrite phase distributes throughout the white austenite matrix in shapes of strips, short rods, and some granular particles, with a directional microstructure distribution. The majority of Al dissolves in the matrix, while precipitates of AlN and other black phases are present. The hardness and corrosion resistance of the steels increase gradually with increasing rolling temperature, and their fracture elongation reaches approximately 47%. The deformation capacity of the steels is greatly improved, with the tensile strength of the steel containing 1% Al (mass fraction) achieving 766 MPa. The fracture surfaces exhibit both large dimples (5-15 m) and small dimples (<5 m). The fracture modes are similar across the three rolling temperatures and all belong to ductile fracture. At the same rolling temperature, the 304 stainless steel with 1.5% Al exhibits better corrosion resistance.

Keywords: metallic materials, warm-rolled, tensile deformation, corrosion resistance, 304 stainless steels

1. Introduction

304 austenitic stainless steel is widely used both domestically and internationally due to its excellent comprehensive properties, finding extensive applications in aerospace, petrochemical, nuclear power, and other industrial sectors. However, harsh service environments such as seawater, soil, and sulfidation make it susceptible to intergranular corrosion and stress corrosion, shortening the service life of components. Consequently, high-aluminum austenitic stainless steel has emerged as a promising alternative, offering resistance to high and low temperatures and improved corrosion performance. The alumina film formed on its surface demonstrates better density and stability compared to conventional chromium oxide films, significantly enhancing corrosion resistance.

Aluminum is a ferrite-forming element. As its content increases, substantial ferrite formation occurs, resulting in a dual-phase microstructure of ferrite and austenite. However, excessive ferrite severely degrades mechanical properties and creep resistance, making composition design critical for high-aluminum stainless steels. Previous research has shown that adding 4.7% Al provides optimal oxidation resistance at 900°C and 1100°C, while 0.7% Al yields high corrosion resistance at 550°C. Our group' s earlier studies demonstrated that Al addition improves high-temperature oxidation resistance and corrosion resistance without reducing room-temperature strength. After hot rolling, the corrosion resistance of 4% Al-containing stainless steel more than doubles compared to Al-free steel. The 12th Five-Year Plan identified "low-temperature rolling technology" as a key energy-saving and emission-reduction initiative. Warm rolling, which involves plastic deformation within the temperature range between cold and hot rolling, aligns with the development trend of microstructure and property control for steel materials. Currently, few reports exist on warm-rolled 304 stainless steel. Therefore, this study investigates the effects of Al addition on the properties of warm-rolled 304 stainless steel and examines the influence of different rolling temperatures on microstructure and properties, providing reliable experimental data and theoretical foundations for industrial application of warm-rolled 304 austenitic stainless steel sheets.

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2. Experimental Methods

Based on the original composition of 304 stainless steel, 1% and 1.5% Al were added to produce the experimental materials listed in . The alloys were melted in an intermediate frequency induction furnace under atmospheric conditions. When the alloy temperature reached 1560°C, it was held for 20 minutes to ensure complete melting and homogenization before being poured into furan resin sand molds.

The cast ingots were surface-cleaned and wire-cut into 80 mm × 35 mm × 5 mm specimens. Based on previous findings that 304 stainless steel exhibits optimal comprehensive mechanical properties at a hot rolling temperature of 1150°C, an MR350 manual rolling mill was used to hot-roll the specimens at 1150°C with a 40% deformation. Inter-pass holding time exceeded 15 minutes, and multi-pass rolling produced 3 mm thick hot-rolled sheets. After removing surface oxide scale, the sheets were warm-rolled at 550°C, 600°C, and 650°C with 50% deformation to final thicknesses of 2.1 mm, 1.5 mm, and 0.9 mm, respectively. The rolled alloys were solution-treated at 1050°C for 30 minutes followed by water quenching.

For hardness testing, warm-rolled sheets were machined into 10 mm × 10 mm specimens and ground smooth with successive grades of abrasive paper. Hardness was measured using an HBRVU-187.5 optical Brinell-Rockwell-Vickers hardness tester with a 298 N load. Six measurements were taken at different locations for each alloy composition, and the average value was reported with measurement error less than 3%.

Room-temperature mechanical properties were tested according to GB/T228-2002. Warm-rolled sheets were machined into standard dumbbell-shaped tensile specimens with a gauge length of 10 mm and cross-sectional area of 3.4 mm². Specimens were ground smooth with abrasive paper ranging from 100 to 1500 grit. Tests were conducted on a computer-controlled electronic universal testing machine using displacement-controlled loading at a strain rate of 0.2 mm/min. The specimen grips were tightened to prevent slippage and ensure accuracy.

Each test was repeated three times under identical conditions. Stress-strain curves were plotted from load-displacement data to determine yield strength and tensile strength.

Fracture morphologies were examined using a JSM-6700F field emission scanning electron microscope to analyze fracture modes and mechanisms under different test conditions. For microstructural observation, solution-treated warm-rolled specimens were ground, polished, and etched (with 50% nitric acid solution) before examination under a Mef3 optical microscope.

Intergranular corrosion resistance was measured by weight loss according to GB4334.3-2000. Specimens were wire-cut into 15 mm × 10 mm × 2 mm samples and sensitized at 650°C for 2 hours followed by air cooling. After grinding with 100–1200 grit abrasive paper, dimensions were measured with vernier calipers to calculate surface area. Samples were ultrasonically cleaned in ethanol for 10 minutes and weighed using an analytical balance with 0.1 mg precision. The corrosion test used (65.0±0.2)% analytical grade nitric acid solution at a dosage of 25–30 mL/cm² based on specimen surface area. The solution was maintained at boiling temperature with circulating water cooling. The test consisted of five 48-hour cycles (total 240 hours), with at least three specimens tested for each alloy composition. After each cycle, corroded samples were removed, rinsed with distilled water to remove corrosion products, dried, and weighed. Results were averaged from three datasets with experimental error less than 3%.

2.1 Microstructure

The warm-rolled microstructures of 304 stainless steel containing 1% Al at different temperatures are shown in [Figure 1: see original paper]. The ferrite phase appears primarily as strips and short rods distributed within the white austenite matrix, accompanied by black phase precipitation. No significant microstructural changes were observed across the three rolling temperatures. [Figure 2: see original paper] shows micrographs of 304 stainless steel with 1.5% Al. Combined with XRD analysis, the microstructure consists mainly of black ferrite and white austenite phases. The ferrite exhibits elongated strip and granular morphologies distributed directionally within the austenite matrix. At rolling temperatures of 550°C and 600°C, ferrite is predominantly elongated strips, while at 650°C it appears as short rods and granules. Additional black precipitates were identified through EPMA area scanning analysis ([Figure 3: see original paper]), revealing that most Al dissolves in the matrix while the black precipitates contain Al, N, and minor C, indicating they are aluminum nitrides and other carbides.

Ferrite content and average grain size were statistically analyzed using IPWIN6.0 software for the high-aluminum 304 stainless steels rolled at different temperatures, with results presented in and . The ferrite volume fraction is significantly lower in the 1% Al steel compared to the 1.5% Al steel. Aluminum is a ferrite solid solution strengthening element, and according to the Cr-equivalent formula, the effect of Al on Cr-equivalent is equivalent to 2.5 times that of Cr. Therefore, higher Al content promotes greater ferrite formation. The average grain size of high-aluminum 304 stainless steel increases with rolling temperature. The effect of temperature on grain size is more pronounced in the 1.5% Al steel than in the 1% Al steel.

Ferrite typically precipitates preferentially at grain boundaries, initially as points and chains that gradually connect into networks. During low-temperature rolling at 550°C, carbon solubility in austenite is low, providing sufficient carbon for ferrite precipitation. As rolling temperature increases to 650°C, carbon solubility in austenite increases slightly, reducing the carbon required for ferrite precipitation. Consequently, ferrite content decreases with increasing rolling temperature. Additionally, the transformation from austenite (packing density 74%) to ferrite (packing density 68%) involves volume expansion due to differences in atomic packing. The statistical results indicate that larger grain sizes obtained at lower rolling temperatures also favor ferrite precipitation.

2.2 Mechanical Properties

The hardness and elongation of 304 stainless steel at different rolling temperatures are shown in [Figure 4: see original paper]. For the 1% Al steel, hardness increases gradually with rolling temperature from 170 HV to 182 HV (a 7% increase). For the 1.5% Al steel, hardness initially increases then decreases with temperature, reaching a maximum of 227 HV—nearly double that of Al-free steel (125 HV). This increase is attributed to the gradual increase in black phase precipitation at the surface with rolling temperature, with more extensive precipitation in the 1.5% Al alloy at 600°C leading to increased hardness. Regarding elongation, the 1% Al steel shows gradual improvement with increasing rolling temperature, while the 1.5% Al steel exhibits a gradual decline, though both maintain approximately 47% elongation. Since Al is a ferrite-forming element, high-aluminum alloys contain greater ferrite volume fractions. Ferrite and austenite have different deformation capacities under external loading. Austenite, with its face-centered cubic structure, has relatively low Peierls-Nabarro stress for dislocation motion, facilitating deformation under stress. Consequently, cracks tend to initiate at ferrite-austenite phase boundaries during tensile testing, causing higher-aluminum alloys to exhibit poorer plastic deformation capacity at the same rolling temperature.

The stress-strain curves and mechanical properties of 304 stainless steel at different rolling temperatures are presented in [Figure 5: see original paper]. Both Al-containing alloys demonstrate good plastic deformation capacity, undergoing elastic-plastic-yielding-fracture processes during tensile testing, with the 1% Al alloy showing substantially improved deformation ability. The yield strength of both alloys changes little with rolling temperature, though the 1.5% Al alloy exhibits higher overall yield strength than the 1% Al alloy. This is because increased Al content promotes greater ferrite formation, and the interstitial carbon and nitrogen atoms in ferrite have higher diffusivity and sufficient time to segregate to dislocation lines, effectively pinning dislocations. Consequently, greater external stress is required to activate dislocation sources for slip, resulting in stronger resistance to plastic deformation. However, the tensile strength of the 1.5% Al alloy is generally lower than that of the 1% Al alloy. This can be attributed to two factors: first, the lower-aluminum alloy contains more austenite, which deforms more readily under stress, increasing strain and enabling higher fracture strength; second, the lower ferrite content reduces the number of phase interfaces, decreasing opportunities and sites for microcrack initiation during post-yield deformation, thereby improving fracture resistance.

The tensile fracture morphologies of 304 stainless steel at different rolling temperatures are shown in [Figure 6: see original paper]. Both alloys exhibit fracture surfaces composed of relatively large equiaxed dimples (5–15 m) surrounded by smaller dimples (<5 m). The fracture modes are similar across the three rolling temperatures, all belonging to ductile fracture. The 1% Al alloy fracture surfaces contain numerous small dimples adjacent to large dimples, with more voids forming during later tensile stages that delay crack propagation, demonstrating strong fracture resistance consistent with the tensile strength analysis. Some flat terraces are also observed in certain regions, indicating a dimple-plus-terrace fracture morphology. In [Figure 6: see original paper]a–c, the number and morphology of large and small dimples are similar, with no obvious fracture platforms, all showing dimple fracture and resulting in comparable deformation capacity and elongation, consistent with [Figure 4: see original paper]. In [Figure 6: see original paper]d–f, the fracture surfaces are dominated by large, deep dimple pits, indicating intense pull-out phenomena during tensile testing and enhanced resistance to deformation.

2.3 Corrosion Resistance

The intergranular corrosion test results for the two Al-containing 304 stainless steels at different rolling temperatures are shown in [Figure 7: see original paper]. The intergranular corrosion rate for both alloys decreases gradually with increasing rolling temperature. At the same rolling temperature, the 304 stainless steel with 1.5% Al exhibits better intergranular corrosion resistance, with corrosion rates of 0.307, 0.302, and 0.237 $g/(m^2 \cdot h)$ at the three temperatures. Intergranular corrosion results from severe chromium depletion at grain edges and boundaries. Al addition promotes ferrite formation, transforming the original single-phase austenite microstructure into a dual-phase structure. Research indicates that the interfacial energy between ferrite and austenite is lower than that of single-phase austenite, and chromium diffusion in ferrite is approximately two orders of magnitude faster than in austenite. Consequently, chromium depletion is compensated, ensuring the durability of the passive film.

Additionally, Al atoms preferentially react with carbon in the microstructure to form compounds, consuming some carbon atoms and hindering carbon diffusion to grain boundaries. This shielding effect reduces chromium carbide formation at grain boundaries, weakening chromium depletion. Furthermore, Al dissolved in the matrix readily forms alumina films. Therefore, the 1.5% Al stainless steel exhibits better corrosion resistance at the same rolling temperature. With increasing rolling temperature, carbon solubility in austenite increases, reducing the amount of carbon available to combine with chromium at grain boundaries and further preventing chromium depletion, thus improving corrosion resistance.

3. Conclusions

(1) In the warm-rolled microstructure of Al-containing 304 stainless steel, the black ferrite phase distributes as strips, short rods, and some granular particles within the white austenite matrix, accompanied by black phase precipitation and showing directional distribution. Most Al dissolves in the matrix, while the black phases contain Al, N, and minor C, identified as aluminum nitrides and carbide-rich precipitates.

(2) The hardness of Al-containing 304 stainless steel increases gradually with rolling temperature, reaching maximum values of 182 HV and 227 HV for the two alloys. With increasing rolling temperature, the elongation of the 1% Al steel increases gradually, while that of the 1.5% Al steel decreases gradually, though both remain approximately 47%. The deformation capacity of Al-containing alloys is substantially improved, with the tensile strength of the 1% Al alloy reaching 766 MPa.

(3) Both alloys exhibit fracture surfaces composed of relatively large equiaxed dimples (5-15 m) and surrounding small dimples (<5 m). The fracture modes are similar across the three rolling temperatures and all belong to ductile fracture.

(4) Corrosion resistance increases with rolling temperature, and the 1.5% Al stainless steel exhibits better corrosion resistance at the same rolling temperature.

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Note: Figure translations are in progress. See original paper for figures.