Low-Temperature Supersaturated Carburization of Austenitic Stainless Steel: Experiments and Thermodynamic-Kinetic Simulations (Postprint)

Authors: Dongsong Rong, Jiang Yong, Gong Jianming

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Abstract

The effects of CO gas concentration on the microstructure, C concentration distribution, surface phase structure, and residual stress of the carburized layer on 316L stainless steel surface in low temperature colossal carburization (LTCC) process were investigated using OM, EPMA, XRD, and IXRD techniques. Based on thermodynamic and kinetic theory, a mass transfer and diffusion model for LTCC was established, and the C concentration and activity distribution in the carburized layer were calculated using DICTRA software and compared with experimental results. The results show that a high-hardness S-phase forms on the surface of 316L stainless steel after LTCC treatment, and compressive residual stress is generated. Additionally, increasing the CO concentration in the carburization process can significantly increase the C concentration in the carburized layer on the stainless steel surface, thereby enhancing its hardness and compressive residual stress. At low C concentrations, the calculated C concentration and activity distributions agree well with experimental results; at high C concentrations, the calculated results are lower due to the reduction of trap sites and the effect of large compressive residual stress.

Full Text

EXPERIMENTAL RESEARCH AND THERMODYNAMIC SIMULATION OF LOW TEMPERATURE COLOSSAL CARBURIZATION OF AUSTENITIC STAINLESS STEEL

RONG Dongsong, JIANG Yong, GONG Jianming
College of Mechanical and Power Engineering, Nanjing Tech University, Nanjing 211816

Correspondent: GONG Jianming, professor, Tel: (025)58139361, E-mail: gongjm@njtech.edu.cn

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Abstract

Low temperature colossal carburization (LTCC) is a novel surface strengthening technology for austenitic stainless steels that significantly increases surface hardness while preserving excellent corrosion resistance by suppressing carbide formation. This study investigates the effects of CO concentration in the carburizing atmosphere on the microstructure, carbon concentration distribution, phase constitution, and residual stress of carburized layers on 316L austenitic stainless steel using optical microscopy (OM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), and X-ray stress analysis (IXRD). Based on thermodynamic theory, a carbon transfer and diffusion model was developed using DICTRA software to calculate carbon concentration and activity distributions in the carburized layer. The results reveal that an S-phase (expanded austenite) forms on the surface of 316L steel after LTCC treatment, accompanied by the generation of compressive residual stress. Increasing CO concentration significantly elevates the carbon concentration in the carburized layer, thereby enhancing both hardness and compressive residual stress. The simulated carbon concentration and activity distributions agree well with experimental results at lower carbon concentrations, but deviate at higher concentrations due to the reduction of trapping sites and the influence of high compressive residual stress.

KEY WORDS low temperature colossal carburization, austenitic stainless steel, DICTRA, carbon concentration, activity

Introduction

Low temperature colossal carburization (LTCC) represents an innovative surface strengthening technology for austenitic stainless steels. The core principle involves reducing the carburizing temperature below 500 °C to prevent carbide precipitation that would compromise corrosion resistance. Research has demonstrated that within the LTCC temperature range, the diffusion rate of carbon in the austenite lattice is 10^4 to 10^5 times faster than that of chromium [1]. Consequently, carbide formation is suppressed during the carburization process, and the carbon that diffuses into the stainless steel surface dissolves in the austenite lattice to form expanded austenite (S-phase) [2], resulting in a significant increase in surface hardness. Qu et al. [3] reported that LTCC treatment increased the surface hardness of 316 stainless steel by 2-4 times and improved wear resistance by 100-fold. Ceschini and Minak [4] found that the fatigue strength of 316L stainless steel increased by 40% after LTCC strengthening. Tokaji et al. [5] investigated the corrosion fatigue performance of LTCC-treated 316 stainless steel in NaCl solution and observed no decrease in fatigue strength compared to air exposure, confirming the excellent corrosion resistance of the low-temperature carburized layer. Li et al. [6,7] and Yang et al. [8] analyzed the microstructure and properties of LTCC-treated 304 and 316 stainless steels, obtaining similar results and proposing an optimal carburizing temperature of 470 °C. In addition to carburizing temperature, key LTCC parameters include gas composition and carburizing time, while the type and content of alloying elements in stainless steel also significantly influence carbon transfer and diffusion.

Elemental diffusion constitutes an irreversible thermodynamic process characterized by a linear relationship between diffusion flux and the thermodynamic force driving it. Based on the law of mass conservation, a time-dependent differential equation for elemental concentration diffusion can be established, which can be solved under appropriate boundary conditions to determine the concentration distribution at any time [9]. The DICTRA (diffusion controlled phase transformation) software, which numerically solves multi-component diffusion equations in conjunction with the Thermo-Calc thermodynamic software, enables analysis of carbon diffusion in multi-component alloys [10]. Compared with other numerical methods, the DICTRA model can investigate the influence of alloying elements on carbon diffusion by introducing interaction parameters. Using DICTRA, Sudha et al. [11], Turpin et al. [12], and Rowan et al. [13] studied carbon concentration distribution, carbide content, and phase transformations in stainless steels after high-temperature carburization, and analyzed the effects of alloying elements on carbon transfer and diffusion. Garcia and Prat [14] simulated the nitriding process of W-Ti-Ta-Nb-Co-C alloys at 1400 °C, with simulation results matching experimental data. Höglund and Ågren [15] analyzed carbon diffusion in multi-component alloys under temperature gradients and corrected the heat transfer coefficients calculated by Okafor et al. [16]. Due to intellectual property protection and other reasons, few studies on key LTCC technical parameters have been reported to date.

In this work, LTCC experiments were conducted on 316L austenitic stainless steel at 743 K using carburizing gases with different CO proportions. The carbon concentration and distribution, surface phase structure, and residual stress of the carburized layers were analyzed. Based on these experiments, a thermodynamic model for carbon transfer and diffusion in austenitic stainless steel was established using DICTRA software to calculate carbon concentration and activity distributions, which were then compared with experimental results.

Experimental Procedures

Materials and Sample Preparation

The 316L austenitic stainless steel used in this study had the following chemical composition (mass fraction, %): C 0.019, Cr 17.87, Ni 10.21, Si 0.248, Mn 1.2, and Fe balance. Samples with dimensions of 10 mm × 10 mm × 5 mm were cut by wire electrical discharge machining, with two samples per group. The specimens were ground with waterproof abrasive paper from 200 to 1500 grit, mechanically polished, ultrasonically cleaned, and dried with cold air for subsequent use.

Surface Activation and Carburization

Due to its high chromium content, 316L stainless steel readily forms a dense passive film on the surface that hinders carbon ingress. Therefore, surface activation treatment is necessary prior to carburization. The activation was performed using HCl/N_2 mixed gas [17] at 523 K for 4 h. Following activation, the temperature was increased to 743 K. Once stabilized, CO/H_2/N_2 mixed gases with CO concentrations (volume fraction) of 15%, 25%, and 30% were introduced for LTCC treatment for 20 h, with corresponding samples designated as S1, S2, and S3. [Figure 1: see original paper] shows a schematic diagram of the LTCC process for austenitic stainless steel. Both surface activation and low-temperature colossal carburization were conducted in a custom-designed experimental system [18].

Characterization Methods

Carburized specimens were electrolytically etched with 10% (volume fraction) oxalic acid solution to reveal the microstructure, and cross-sectional morphologies of the carburized layers were observed using an ImagerA1M optical microscope (OM). Carbon concentration distribution in the carburized layer was quantitatively analyzed using an EPMA-1610 electron probe microanalyzer (EPMA). Surface phase structure was examined using a D max/RB X-ray diffractometer (XRD) with a scanning range of 30°–80°. Surface residual stress was measured using an Ixrd Combo X-ray stress analyzer (IXRD) according to GB/T 7704-2008, with the (311) diffraction plane selected and diffraction wavelength $\lambda = 2.10314$ nm.

2 Results

Microstructure and Carbon Concentration Distribution

[Figure 2: see original paper] and [Figure 3: see original paper] show cross-sectional OM images and carbon concentration profiles of 316L stainless steel after LTCC treatment with different CO concentrations. When the CO concentration was 15%, the carburized layer thickness was approximately 4 mm, with surface carbon concentration increasing from 0.019% (mass fraction, same below) to 0.78%. When the CO concentration increased to 30%, the carburized layer thickness grew to 30 mm, and the surface carbon concentration further increased to 2.58%, which is about 800 times the equilibrium solubility of 316L stainless steel at 743 K [19]. In this state, carbon exists in a "quasi-equilibrium" condition within the austenite lattice, hence the LTCC process is also termed low-temperature quasi-equilibrium carburization. Additionally, after electrolytic etching with 10% oxalic acid solution, the austenite grain boundaries in the stainless steel substrate were revealed, while the carburized layer showed no such features, indicating superior corrosion resistance of the carburized layer compared to the substrate.

Phase Structure and Residual Stress

[Figure 4: see original paper] presents XRD spectra of the 316L stainless steel substrate and sample S3 surface. Comparison reveals that sample S3 retained the austenite phase, but its austenite characteristic peaks shifted to lower angles. This shift occurs because carbon dissolved in the austenite lattice causes lattice expansion and increased interplanar spacing, forming the expanded austenite phase (S-phase). According to Bragg' s equation ($\lambda = 2d \sin\theta$, where d is interplanar spacing and θ is diffraction angle), the diffraction angle decreases.

IXRD measurements indicated that the surface residual stresses of samples S1, S2, and S3 were -335 MPa, -595 MPa, and -1735 MPa, respectively. All specimens developed compressive residual stresses parallel to the surface. These compressive stresses primarily result from carbon ingress and its gradient distribution. The austenite lattice expansion caused by carbon dissolution in the carburized layer is constrained by the uncarburized core, generating compressive residual stress. As carbon concentration increases, the degree of lattice expansion increases, leading to more pronounced constraint effects and higher compressive residual stress. [Figure 5: see original paper] shows the relationship between compressive residual stress and carbon concentration, which follows a linear relationship: $\sigma_c = -743.9 + 177.93c$ (where σ_c is compressive residual stress in MPa and c is carbon concentration in mass %).

Thermodynamic Modeling

3.1 Geometric Model

As shown in [Figure 2: see original paper], the low-temperature colossal carburized layer is relatively uniform, with carbon concentration exhibiting gradient distribution only along the depth direction. Therefore, the LTCC problem can be simplified to a one-dimensional model. [Figure 6: see original paper] illustrates the geometric schematic of the LTCC model. The model length was set to 40 mm, with nodes distributed geometrically along the depth direction. The number of nodes was 130, and the distance ratio was 0.9. As indicated by [Figure 4: see original paper], no phase transformation occurred in the supersaturated carburized layer, so both the carburized layer and 316L stainless steel substrate were defined as fcc structure.

3.2 Governing Equations

The LTCC process can be regarded as a problem of active carbon mass transfer at the austenitic stainless steel interface and subsequent diffusion into the steel interior. According to irreversible thermodynamic analysis [20], carbon diffusion is governed by Fick' s second law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D_c \frac{\partial c}{\partial z}\right)$$

where D_c is the carbon diffusion coefficient (m^2/s) and z is the depth from the steel surface (m).

The boundary condition at the steel surface is given by:

$$J = \beta(a_g - a_s)$$

where β is the carbon mass transfer coefficient (m/s), and a_g and a_s are the carbon activities in the carburizing gas and at the austenitic stainless steel surface (%), respectively.

The gas carbon activity a_g depends on the carburizing temperature and partial pressures of components involved in active carbon decomposition reactions. For $CO/H_2/N_2$ mixed gas, a_g can be expressed as [21]:

$$a_g = \frac{p_{\mathrm{CO}} \cdot p_{\mathrm{H2}}}{p_{\mathrm{H2O}} \cdot K}$$

where K is the equilibrium constant, and p_{CO}, p_{H2}, and p_{H2O} are the partial pressures of CO, H_2, and H_2O after gas equilibrium (10^5 Pa), respectively. However, studies [22] have identified over 180 simultaneous reactions in the carburizing gas, making it impossible to obtain accurate a_g from this equation alone. Moreover, the low temperature prevents measurement using infrared analyzers or oxygen probes. Based on our previous experimental results, when carburizing time exceeds 15 h, the surface carbon concentration changes very little with further time extension, indicating that mass transfer reaches dynamic equilibrium after 15 h and the surface carbon activity becomes essentially equal to the gas carbon activity. [Figure 7: see original paper] shows the relationship between carbon concentration and activity in 316L stainless steel at 743 K calculated by DICTRA, yielding a_g values of 0.44%, 0.57%, and 3.48% for CO concentrations of 15%, 25%, and 30% in $CO/H_2/N_2$ mixed gas, respectively.

Gao et al. [23], Edenhofer [24], and Gupta et al. [25] proposed several numerical formulas for calculating carbon mass transfer coefficients. However, like gas carbon activity, mass transfer coefficients obtained solely through numerical calculation have large errors and must be determined experimentally. Based on experimental results, Gao et al. [26] proposed that the surface carbon concentration is a function of mass transfer coefficient, diffusion coefficient, and carburizing time:

$$\frac{c_s - c_0}{c_g - c_0} = 1 - \exp\left(\frac{\beta^2 t}{D_c^2}\right) \operatorname{erfc}\left(\frac{\beta\sqrt{t}}{D_c}\right)$$

where c_s is the surface carbon concentration of the carburized layer (%), c_0 is the original carbon concentration of 316L stainless steel (%), c_g is the carbon potential of the carburizing gas (%), and t is carburizing time (s). The c_g values equal the surface carbon concentrations of samples S1, S2, and S3: 0.79%, 0.93%, and 2.58%, respectively. To calculate the mass transfer coefficient, additional short-duration LTCC experiments (12 min) were conducted under the same CO concentrations (samples S4, S5, and S6), yielding surface carbon concentrations c_s of 0.13%, 0.16%, and 1.1% as measured by EPMA.

The carbon diffusion coefficient D_c depends on carburizing temperature, alloying elements, and carbon concentration. At 743 K, D_c values are 4.5×10^{-17} and 6.53×10^{-16} m^2/s for carbon concentrations of 0.019% (0.09 at%) and 2.15% (10 at%), respectively [27]. According to the Arrhenius equation:

$$D_c = D_0 \exp\left(-\frac{Q}{RT}\right)$$

where D_0 is the diffusion constant (m^2/s), Q is the diffusion activation energy (J/mol), and R is the gas constant (J/(mol · K)). At 743 K, the corresponding D_c values are 1.875×10^{-16} and 2.72×10^{-15} m^2/s. The relationship between carbon diffusion coefficient and carbon concentration can be expressed as [27]:

$$D_c = D_0 \exp\left(\frac{kc}{c_{\max}}\right)$$

where D is the carbon diffusion coefficient in 316L stainless steel (m^2/s), k is a proportional constant, and $c_{\max}$ is the limiting carbon concentration at a specific temperature (%). According to literature [20], the limiting solubility of 316L stainless steel at 743 K is 2.47%, giving $k = 3.07$. Further calculation yields surface D_c values of 4.85×10^{-16}, 5.72×10^{-16}, and 3.49×10^{-16} m^2/s for samples S4, S5, and S6, respectively. Substituting c_g, c_s, c_0, D_c, and t into the equation gives mass transfer coefficients β of 1.1×10^{-10}, 1.24×10^{-10}, and 7.58×10^{-10} m/s for CO concentrations of 15%, 25%, and 30%, respectively.

In the DICTRA framework, D_c is expressed in terms of atomic mobility. Based on absolute reaction rate theory, D_c can be written as:

$$D_c = LRT$$

where L is a phenomenological parameter that relates carbon diffusion flux to its driving force. For interstitial carbon atoms:

$$L = y_{\mathrm{va}} M_C$$

where y_{va} is the vacancy fraction on the sublattice and M_C is carbon mobility:

$$M_C = M_0 \exp\left(-\frac{Q}{RT}\right)$$

where M_0 is the frequency factor (s^{-1}) and Q is the activation enthalpy (J). Both M_0 and Q are functions of material composition, temperature, and pressure. In the DICTRA approach, they can be transformed into [28]:

$$RT \ln M_0 = \sum_i x_i (RT \ln M_0)_i + \sum_i \sum_{j>i} x_i x_j \left[\sum_r (x_i \Omega_{ij}^r)\right]$$

where $(RT \ln M_0)_i$ represents the value in pure component i, Ω_{ij}^r are interaction parameters between components i and j, and x_i and x_j are mole fractions of components i and j. According to the Jönsson model [29], the magnetic factor Ω can be expressed as:

$$\Omega = \Phi_i \Phi_j$$

where Φ values are given by $\Phi_i = \exp(6)\exp(z)$, with z representing the magnetic ordering state and a being a constant (for fcc lattice materials).

4 Discussion

4.1 Carbon Concentration and Activity Distribution

The simulated carbon concentration and activity distributions are presented in [Figure 3: see original paper] and [Figure 8: see original paper]. For samples S1 and S2, the simulated carbon concentration and distribution patterns agree well with experimental results. However, for sample S3, the simulated carbon concentration is slightly lower than experimental values, particularly in regions with high carbon content. This discrepancy arises because the carbon diffusion coefficient in multi-component alloys depends not only on alloying elements but also on stress state and carbon concentration. Experimental results demonstrate the presence of compressive residual stress σ_c in the LTCC-treated layer, which increases with carbon concentration. According to Yang' s model [30], the relationship between carbon diffusion coefficient and σ_c is:

$$D' = D \exp\left(-\frac{\sigma_c V_C}{RT}\right)$$

where D' is the carbon diffusion coefficient under stress and V_C is the partial molar volume of carbon in the metal. This equation shows that D' increases with the absolute value of σ_c. Parascandola et al. [31] proposed a "trap-detrapping" model for carbon diffusion in austenitic stainless steel based on Möller et al.' s work [32]. This model considers each Cr atom as a carbon trap site due to its strong affinity with carbon. As carbon penetrates the stainless steel, these trap sites become occupied and decrease in number, leading to increased carbon diffusion rates. The DICTRA model does not account for these two factors affecting the diffusion coefficient, resulting in underestimation of the calculated results for sample S3.

4.2 Surface Carbon Concentration

[Figure 9: see original paper] shows the variation of surface carbon concentration with time for samples S1, S2, and S3. The calculated surface carbon concentrations are in reasonable agreement with experimental measurements. However, the time required to reach stable surface carbon concentration in the simulations is much shorter than in actual experiments. This difference occurs because, in addition to carburizing temperature, gas composition, and alloying elements, factors such as gas flow rate [33], pressure, sample geometry [21], and surface morphology [34] also affect carbon mass transfer at the stainless steel surface, significantly increasing the time needed to reach equilibrium surface carbon concentration.

Conclusions

(1) After LTCC treatment with $CO/H_2/N_2$ mixed gas, 316L austenitic stainless steel forms a colossal carburized layer without carbide precipitation, with an expanded austenite phase (S-phase) structure.

(2) As the CO concentration in $CO/H_2/N_2$ mixed gas increases, both the carbon concentration and thickness of the low-temperature colossal carburized layer increase progressively. At 30% CO concentration, the surface carbon concentration of 316L stainless steel reaches 2.58% and the carburized layer thickness is approximately 30 mm, generating compressive residual stress exceeding 1700 MPa.

(3) The thermodynamic model for low-temperature colossal carburization of austenitic stainless steel, established based on thermodynamic theory, can satisfactorily predict the carbon concentration and activity distributions in the carburized layer. At higher carbon concentrations, the simulation results are slightly lower than experimental values due to the reduction of trap sites and the presence of compressive residual stress.

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