ChinaRxiv

AI translation · View original & related papers at
chinarxiv.org/items/chinaxiv-202303.00524

Numerical Analysis of Low-Temperature Surface Carburization of 316L Austenitic Stainless Steel (Postprint)

Authors: Peng Yawei, Gong Jianming, Rong Dongsong, Jiang Yong, Fu Minghui, remaining fruit

Date: 2023-03-19T00:00:00+00:00

Abstract

Low-temperature surface carburization experiments were conducted for surface strengthening of 316L austenitic stainless steel, and the depth profile of carbon concentration within the carburized layer of post-carburized specimens was measured. A kinetic model based on the “trap-detrap” mass transfer mechanism was established, which postulates that chromium atoms exert a trapping effect on carbon atoms during carbon diffusion. Using this model, the depth profile of carbon concentration in the carburized specimens was calculated and compared with experimental results. The results demonstrate that the experimentally measured carbon concentration depth profile exhibits a convex shape, which differs from the predictions of simple Fick’ s law. In contrast, the calculations based on the “trap-detrap” model show good agreement with experimental data, indicating that the trapping effect plays a significant role in carbon diffusion. Chromium atoms reduce the carbon diffusion coefficient through their trapping effect on carbon atoms, and fitting of the experimental data yielded a detrapping activation energy of carbon of 165 kJ/mol. The proposed model is only applicable to low-temperature carburization without carbide precipitation and does not account for the effects of diffusion-induced stress.

Full Text

Preamble

Numerical Analysis of Low-Temperature Surface Carburization for 316L Austenitic Stainless Steel

PENG Yawei, GONG Jianming, RONG Dongsong, JIANG Yong, FU Minghui, YU Guo

School of Mechanical and Power Engineering, Nanjing Tech University, Nanjing 211816

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

Supported by National Natural Science Foundation of China (No. 51475224) and Natural Science Foundation of Jiangsu Higher Education Institutions of China (No. 14KJA470002)

Manuscript received 2015-05-07, in revised form 2015-07-14

Abstract

Low-temperature surface carburization has proven to be one of the most effective techniques for improving the mechanical properties of 316-type austenitic stainless steel (Fe-Cr-Ni alloy), including surface hardness, fatigue resistance, and wear resistance. It is well known that carbon diffusion in austenitic stainless steel is a very complicated process and still not fully understood. Therefore, it is of great importance to elucidate the carbon diffusion mechanism in steel and establish a model that can predict the carbon concentration along the depth direction under any given carburization conditions. Studies in recent years reveal that trapping effects should be considered in carbon diffusion in austenitic steels at low temperature. In this work, low-temperature surface carburization treatment was carried out on 316L austenitic stainless steel, and the carbon concentration along the depth direction was measured. A kinetic model based on the "trapping-detrapping" mass transport mechanism for simulating the carbon fraction-depth profile was developed. This model considered that the diffusion of carbon occurs under the influence of trap sites formed by local chromium atoms. The calculated carbon concentration was then compared to the experimental results to check the validity of the model. The results show that: (1) in low-temperature-carburized 316L austenitic stainless steel, the carbon fraction-depth profile exhibits a plateau-type shape which is not consistent with the standard analytic solution of the diffusion equation (Fick' s law of diffusion); (2) the carbon fraction-depth profile based on the "trapping-detrapping" model is in good agreement with the experimental carbon fraction-depth profile, which indicates that the trapping effect plays an important role in carbon diffusion; (3) carbon diffusivity decreases due to the trapping effect of Cr atoms, and the detrapping energy of carbon deduced from fitting experimental data is 165 kJ/mol; (4) the proposed model can only be used to describe carbon diffusion in austenitic stainless steel during low-temperature surface carburization without chromium carbide precipitation. In addition, the influence of stresses induced by incorporating carbon into the austenite lattice on the carbon transport mechanism is not included in the trapping-detrapping model.

Key Words austenitic stainless steel, surface strengthening, low-temperature surface carburization, carbon diffusion, trapping-detrapping model

Introduction

Austenitic stainless steel has become an indispensable material in industrial production due to its excellent comprehensive properties and corrosion resistance. However, its relatively low surface strength and hardness severely limit its service life in industrial applications, particularly in fields such as petrochemical processing, food production, chemicals, marine engineering, and medicine, where materials are required to possess not only outstanding corrosion resistance but also high surface hardness, load-bearing capacity, and wear resistance to ensure reliable operation of equipment and components, thereby improving production efficiency and extending service life. Consequently, surface strengthening of austenitic stainless steel has long been a hot research topic, though achieving surface strengthening while maintaining its original excellent comprehensive properties and superior corrosion resistance has remained fundamentally unresolved.

Over the past decade, developed countries including the United States, Europe, and Japan have devoted significant efforts to developing a novel surface strengthening method for stainless steel known as low-temperature gas-phase carburization (LTC). This method involves carburizing austenitic stainless steel below the theoretical formation temperature of chromium carbides (520–550 °C), resulting in a carburized layer with high carbon concentration but without chromium carbide precipitation. This layer structure, designated as the carbon S-phase or expanded austenite (gC), exhibits high hardness, good wear resistance and toughness while retaining excellent corrosion resistance, thereby achieving the coexistence of surface strengthening and corrosion resistance. However, since low-temperature surface carburization is a relatively recent development, many aspects of research remain inadequate. Most studies on the diffusion of active carbon atoms during the carburization process have relied on simple Fick’ s second law for analyzing carbon concentration and distribution. While this theory has proven effective for conventional high-temperature carburization, it is less satisfactory for low-temperature carburization problems, a limitation that has attracted attention from scholars worldwide who have attempted to propose more reasonable models to predict carbon diffusion during low-temperature carburization, thereby optimizing the process to achieve optimal strengthening effects.

In reality, during low-temperature carburization surface strengthening of stainless steel, the carbon concentration distribution in the diffusion layer is non-uniform, which generates significant compressive residual stresses on the workpiece surface and improves fatigue strength. Both the surface compressive residual stress and hardness after carburization can be calculated from the carbon concentration, making prediction of carbon concentration distribution in low-temperature carburized layers critically important. In recent years, researchers analyzing nitrogen diffusion in low-temperature plasma nitriding surface strengthening of stainless steel have considered the influence of Cr atom traps, and based on this work, Parascandola et al. proposed a “trapping-detrapping” diffusion model that showed good agreement between calculated and experimental results, supporting the special role of “trap” Cr atoms in nitrogen atom diffusion. However, few reports have considered the influence of “traps” on diffusion during low-temperature surface carburization, and no scholar has yet proposed a “trapping-detrapping” diffusion model for carbon.

Therefore, this study establishes a kinetic model for carbon diffusion based on the “trapping-detrapping” mass transport mechanism to analyze the distribution pattern of carbon concentration along the diffusion layer in austenitic stainless steel after low-temperature (470 °C) gas carburization, investigates the trapping effect of Cr atoms on carbon atoms during carbon diffusion, and compares the calculated results with actual experimental results to verify the validity of the model.

Experimental Materials and Methods

The experimental material was 316L austenitic stainless steel with a chemical composition (mass fraction, %) of: C 0.03, Cr 17.54, Ni 10.10, Mo 2.12, Mn 1.43, Si 0.55, Fe balance. The material was machined into block samples measuring 10 mm × 10 mm × 6 mm. Prior to experiments, samples were ground progressively with sandpaper, cleaned ultrasonically with acetone for degreasing, dried, and placed in a self-built low-temperature carburization apparatus consisting primarily of a carburization furnace and associated gas piping.

The basic process for low-temperature carburization of 316L austenitic stainless steel was as follows: First, samples were placed in the carburization furnace, the furnace was evacuated, and N_2 was introduced repeatedly to replace the air inside. The furnace temperature was then raised to the activation temperature of 200–300 °C, and activation gas (a mixture of HCl and N_2 with a volumetric flow ratio of 1:3) was introduced to activate the sample surfaces and remove the passive layer for 2–4 hours. After activation, HCl gas supply was stopped, the temperature was raised to the carburization temperature of 470 °C, and carburization gas (a mixture of CO, H_2, and N_2 with a volume ratio of 1:1:2) was introduced for carburization times of 10, 20, and 30 hours.

After carburization, samples were furnace-cooled to room temperature, removed, and ultrasonically cleaned with acetone. The microstructure of carburized samples was observed using an AXIO Imager.Alm optical microscope (OM). Surface carbide precipitation was analyzed using an ARL X’ TRA X-ray diffractometer (XRD) with Cu target, scanning range of 30°–90°, and scanning rate of 10°/min. Carbon concentration distribution along the depth direction of carburized samples was measured using an EPMA-1610 electron probe microanalyzer (EPMA) with line scanning on cross-sections and wavelength dispersive spectrometer (WDS) for X-ray detection.

Experimental Results

[Figure 1: see original paper] shows cross-sectional OM images of 316L austenitic stainless steel before carburization and after gas carburization at 470 °C for 10, 20, and 30 hours. The images reveal that after different carburization times, all samples obtained a uniform bright hardened layer that was distinctly different from the austenitic microstructure of the core. The carburized layer thicknesses after 10, 20, and 30 hours were approximately 15, 25, and 30 m, respectively, as shown in Figures 1b–d.

[Figure 2: see original paper] presents XRD spectra of 316L austenitic stainless steel before carburization and after carburization at 470 °C for different times. The spectra show that no new diffraction peaks appeared after carburization, indicating no carbide precipitation during the process. Additionally, all diffraction peaks shifted to lower angles compared to those before carburization, primarily because supersaturated dissolution of carbon atoms in austenite caused expansion of the face-centered lattice constant and interplanar spacing in the surface layer.

[Figure 3: see original paper] shows the carbon concentration distribution along the depth direction in the surface layer of 316L austenitic stainless steel after low-temperature surface carburization at 470 °C for 10, 20, and 30 hours. After 10 hours of carburization, the carbon distribution along the depth direction was basically consistent with the analytical solution of the standard Fick equation. However, with increasing carburization time, the carbon distribution in the diffusion layer exhibited a typical "convex" shape, inconsistent with the simple Fick equation solution. As carburization time increased, both the carbon concentration level in the carburized layer and the layer thickness increased, with thicknesses of approximately 15, 25, and 30 m after 10, 20, and 30 hours, respectively. These results are consistent with microstructural observations and similar to experimental measurements reported by Michal et al.

Trapping-Detrapping Model

Based on the fundamental "trapping-detrapping" theory, this study modifies the basic theoretical model by incorporating carburizing gas absorption boundary conditions to establish a "trapping-detrapping" diffusion model for carbon during low-temperature surface carburization of stainless steel. In this model, carbon atoms as diffusing species may occupy two types of octahedral interstitial sites: trap positions (associated with Cr atoms) where carbon atoms are difficult to escape due to high activation energy barriers, and diffusion positions where activation energy barriers are low and carbon atoms can easily escape. The model is based on the following assumptions: (1) Cr atoms can form traps for carbon atoms, and there is only one type of trap; (2) trap concentration is constant and independent of depth and time; (3) each trap can capture only one carbon atom; (4) detrapping energy is independent of the fraction of occupied traps; (5) local equilibrium exists between carbon in free positions and carbon in trap positions; (6) trapping and detrapping are diffusion-controlled and follow first-order kinetics.

The mass diffusion equations for carbon are as follows:

$$\frac{\partial C_d}{\partial t} = D\frac{\partial^2 C_d}{\partial x^2} - k_{d\to t}C_d + k_{t\to d}C_t \quad (1) \tag{1}$$

$$\frac{\partial C_t}{\partial t} = k_{d\to t}C_d - k_{t\to d}C_t \quad (2) \tag{2}$$

$$C = C_d + C_t \quad (3) \tag{3}$$

Assuming only inward diffusion, the boundary conditions can be expressed as:

$$-D\frac{\partial C_d}{\partial x}\bigg|_{x=0} = b(C_P - C_d|_{x=0}) \quad (4) \tag{4}$$

$$k_{d\to t} = 4\pi R_t D H_t \quad (5) \tag{5}$$

$$k_{t\to d} = 4\pi R_t D H_0 \exp\left(-\frac{Q_t}{RT}\right) \quad (6) \tag{6}$$

where variable x represents the diffusion distance of carbon atoms from the outer surface, t represents carburization time, D represents the diffusion coefficient (for carbon in diffusion positions), $k_{d\to t}$ and $k_{t\to d}$ represent trapping and detrapping coefficients, respectively; S represents the influence of traps. C_t and C_d represent carbon concentration at trap positions and diffusion positions, respectively, and C represents total carbon concentration; b represents the mass transfer coefficient; C_P represents carbon potential; H_t represents trap concentration; R_t represents capture radius at trap positions; H_0 represents solvent atom concentration; D_0 represents diffusion constant; Q_d represents diffusion activation energy; Q_t represents detrapping activation energy; R represents the ideal gas constant; T represents carburization temperature.

In these equations, the $D\partial^2 C_d/\partial x^2$ term in equation (1) and the $D\partial C_d/\partial x$ term in equation (4) represent the inward diffusion process of carbon in austenitic stainless steel. The first term $k_{d\to t}C_d$ in equations (2) and (5) represents the transition of carbon from diffusion positions to trap positions, while the second term $k_{t\to d}C_t$ represents the transition from trap positions to diffusion positions. The first term in equation (4) represents the carbon absorption term.

Equations (1)-(6) can be solved numerically using the finite difference method. Therefore, the carbon diffusion relationship can be transformed into the following form using the Crank-Nicolson finite difference method:

For the surface layer ($i = 0$):

$$C_d^{i+1} = C_d^i + \frac{D\Delta t}{2h^2}\left(C_d^{i+1} - 2C_d^i + C_d^{i-1}\right) - k_{d\to t}\Delta t C_d^i + k_{t\to d}\Delta t C_t^i \quad (10)$$

For other layers ($i > 0$):

$$C_d^{i+1} = C_d^i + \frac{D\Delta t}{2h^2}\left(C_d^{i+1} - 2C_d^i + C_d^{i-1}\right) - k_{d\to t}\Delta t C_d^i + k_{t\to d}\Delta t C_t^i \quad (11)$$

where superscript i represents nodes on the finite difference grid and h is the distance between two adjacent nodes. Equations (10)-(13) can be integrated over the time interval from t to $t + \Delta t$ using the finite difference method. The time step Δt should be sufficiently small to prevent instability in the calculated results.

Theoretical Model Results and Discussion

To verify the accuracy of the proposed model, the experimental results were fitted by numerically solving equations (1)-(6). All parameters except Q_t could be obtained directly or indirectly from published literature, while Q_t could be determined by fitting the experimental carbon concentration profiles along the carburized layer depth. R_t can be considered as the lattice constant of austenitic stainless steel, i.e., $R_t = 0.37 \times 10^{-9}$ m, $H_0 = 7.29 \times 10^{28}$ m^{-3}, $D_0 = 2.0 \times 10^{-5}$ m^2/s, $Q_d = 140$ kJ/mol. At 470 °C, this yields $D = 3.6 \times 10^{-15}$ m^2/s, which is larger than the diffusion coefficient actually measured by Agarwala et al. at 470 °C ($D = 1.9 \times 10^{-16}$ m^2/s). This discrepancy arises because the former does not account for the influence of Cr elements, whose presence reduces the diffusion coefficient of carbon in austenite.

Ernst et al. found that extending low-temperature surface carburization time leads to precipitation of Cr_7C_3, indicating that trapping one carbon atom requires 2–3 Cr atoms. Since the Cr content in 316L austenitic stainless steel is approximately 18% (atomic fraction), the trap concentration should be about 8%. Additionally, Ågren found that in austenitic stainless steel, when carbon concentration exceeds 8%, the carbon diffusion coefficient increases significantly. Therefore, in this work, the trap concentration was taken as 8%, i.e., $H_t = 8\%$.

Since $C_P = a_c \cdot C_s$, where a_c is carbon activity in austenite (effective concentration) and C_s is the saturated carbon content in austenite at a given temperature, the equilibrium carbon concentration (solubility) of 316L stainless steel at 470 °C under CO-H_2-N_2 atmosphere can be obtained from Sharghi-Moshtaghin et al. as $C_s = 11.5\%$ (atomic fraction). The activity a_c can be calculated using the formula given in reference [24]:

$$a_c = \frac{P_{CO}}{P_{CO} + P_{H_2O}} \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

where P_{CO}, P_{H_2}, and P_{H_2O} are the partial pressures of CO, H_2, and water vapor after carburization equilibrium, respectively. Calculation yields $a_c = 1$, thus $C_P = 11.5\%$.

From references [25,26], the mass transfer coefficient b can be obtained as:

$$b = 6.31 \times 10^{-6} \exp\left(-\frac{22350}{T}\right) + 5.6 \times 10^{-4} \exp\left(-\frac{12900}{T}\right)$$

At 470 °C, $b = 2.4 \times 10^{-10}$ m/s.

Since Q_t cannot be obtained directly or indirectly from literature, its value is difficult to determine. Therefore, different Q_t values were tested in equations (1)-(6), and it was found that when $Q_t = 165$ kJ/mol, the experimental carbon concentration profiles along the carburized layer depth were best fitted.

Using the determined parameters in equations (1)-(6), the carbon concentration distributions along the carburized layer depth for carburization times of 10, 20, and 30 hours were calculated using the finite difference method and compared with experimental measurements in [Figure 4: see original paper]. After 10 hours of carburization, the carbon concentration distribution along the depth direction did not show the obvious plateau shape observed after 20 and 30 hours, but instead decreased rapidly with increasing depth, similar to results from simple Fick’ s law. Ernst et al. explained that due to the high affinity between carbon and chromium atoms, chromium carbides do not form at low temperatures; instead, Cr atoms form traps for carbon atoms through chemical bonding influences. When carbon concentration is below the trap concentration, carbon atoms are trapped by Cr atoms, resulting in a smaller carbon diffusion coefficient and rapid decrease in carbon concentration with increasing depth. However, as carburization time increases, when surface carbon concentration exceeds the trap concentration set by Cr atoms, the carbon diffusion coefficient increases accordingly. With increasing depth, surface carbon concentration decreases slowly, and the distribution curve exhibits a typical convex shape, inconsistent with simple Fick’ s law results, while the theoretical calculations based on the trapping-detrapping model agree well with experimental results.

[Figure 5: see original paper] shows the calculated and experimentally measured carbon concentrations in 316L austenitic stainless steel after 20 hours of carburization, where total carbon concentration $C = C_t + C_d$. The distribution of C_d (carbon at diffusion sites) along the depth direction shows a typical diffusion profile shape (according to simple Fick’ s law), while C_t (carbon at trapping sites) and total carbon concentration exhibit plateau-type behavior that simple Fick’ s law cannot capture, demonstrating that trapping effects indeed play an important role in carbon diffusion.

The influence of Q_t on carbon concentration distribution after 20 hours of carburization in 316L austenitic stainless steel is shown in [Figure 6: see original paper]. Q_t depends primarily on austenitic stainless steel properties such as composition, mechanical stress, and lattice parameters. As shown in the figure, when detrapping activation energy decreases, trapping effects weaken, carburized layer thickness increases, and the diffusion process is enhanced, resulting in a concave carbon concentration distribution along the depth direction—a typical diffusion profile shape (according to simple Fick' s law). Conversely, when detrapping activation energy increases, trapping effects strengthen, carburized layer thickness decreases, and the carbon concentration distribution along the depth direction shows an obvious plateau. Thus, due to the presence of Cr atoms, the actual carbon diffusion coefficient throughout the carburization process will be less than 3.6×10^{-15} m^2/s, consistent with findings by Agarwala et al. and Farkas and Delgado that Cr element presence reduces carbon diffusion coefficient in austenite. When detrapping activation energy is 165 kJ/mol, the calculated carbon concentration distribution best matches the experimentally obtained distribution. At this value, the detrapping activation energy of carbon in 316L austenite is 25 kJ/mol greater than the diffusion activation energy, i.e., 0.26 eV.

Conclusions

(1) After low-temperature surface carburization of 316L austenitic stainless steel, experimentally measured carbon concentration distributions along the carburized layer depth exhibit plateau-type behavior that cannot be accurately described by classic Fick' s second law.

(2) By establishing a trapping-detrapping diffusion model, the calculated carbon concentration distributions along the carburized layer depth agree well with experimental measurements, indicating that trapping-detrapping is one of the important mechanisms in carbon diffusion during low-temperature surface carburization.

(3) During carbon diffusion, Cr atoms exert a trapping effect on carbon atoms that reduces carbon diffusivity, and fitting experimental data yields a carbon detrapping activation energy of 165 kJ/mol.

(4) The proposed model is only applicable to low-temperature carburization without carbide precipitation. Additionally, since carbon diffusion into the austenite lattice generates stresses, the influence of diffusion-induced stresses has not yet been incorporated into this model.

References

[1] Heuer A H, Qu J, O' Donnell L. Encyclopedia of Tribology. New York: Springer US, 2013: 2017
[2] Lo R H, Shek C H, Lai J K L. Mater Sci Eng, 2009; R65: 39
[3] Leyland A, Lewis D B, Stevenson P R, Matthews A. Surf Coat Technol, 1993; 62: 608
[4] Lewis D B, Leyland A, Stevenson P R, Matthews A. Surf Coat Technol, 1993; 60: 416
[5] Karabelchtchikova O, Sisson R D. J Phase Equilib Diff, 2006; 27:
[6] Gu X T, Michal G M, Ernst F, Kahn H, Heuer A H. Metall Mater Trans,

2014; 45A: 3790
[7] Wang Y F, Gong J M, Rong D S, Gao F. Acta Metall Sin, 2014; 50: (王艳飞, 巩建鸣, 荣冬松, 高峰. 金属学报, 2014; 50: 409)
[8] Agarwal N, Kahn H, Avishai A, Michal G, Ernst F, Heuer A H. Acta Mater, 2007; 55: 5572
[9] Michal G M, Ernst F, Kahn H, Cao Y, Oba F, Agarwal N, Heuer A H. Acta Mater, 2006; 54: 1597
[10] Christiansen T, Somers M A J. Mater Sci Eng, 2006; A424: 181
[11] Möller W, Parascandola S, Telbizoiva T, Gunzel G, Richter E. Surf Coat Technol, 2001; 73: 136
[12] Zhang Z P, Li P. Vacuum, 2014; 101: 321
[13] Parascandola S, Möller W, Williamson D L. Appl Phys Lett, 2000; 76: 2194
[14] Rong D S, Gong J M, Jiang Y, Geng L Y. Chin Pat, 103323355 A, 2013
[15] Jackson W B, Tsai C C. Phys Rev, 1992; 45B: 12
[16] Abrasonis G, Rivière J P, Templier C, Pranevičius L, Barradas N P. J App Phys, 2005; 97: 124906
[17] Sun Y, Chin L Y. Surf Eng, 2002; 18: 443
[18] Liu W J, Brimacombe J K, Hawbolt E B. Acta Metall Mater, 1991; 39: 2373
[19] Agarwala R P, Naik M C, Anand M S, Paul A R. J Nucl Mater, 1970; 36: 41
[20] Farkas D, Delgado J. Scr Metall, 1983; 17: 261
[21] Ernst F, Li D Q, Kahn H, Harold, Michal G M, Heuer A H. Acta Mater, 2011; 59: 2268
[22] Agren J. Scr Metall, 1986; 20: 1507
[23] Sharghi-Moshtaghin R, Kahn H, Ge Y, Gu X, Martin F J, Natishan P M, Rayne R J, Michal G M, Ernst F, Heuer A H. Metall Mater Trans, 2010; 41A: 2022
[24] Grabke H J. Mater Corros, 2003; 5: 736
[25] Raic K T. Scand J Metall, 1993; 22: 50
[26] Munts V A, Baskakov A P. Met Sci Heat Treat, 1983; 25: 98
[27] Ernst F, Avishai F, Kahn H, Gu X, Michal G M, Heuer A H. Metall Mater Trans, 2009; 40A: 1768
[28] Ernst F, Cao Y, Michal G M, Heuer A H. Acta Mater, 2007; 55:

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

Source: ChinaXiv —Machine translation. Verify with original.