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Improved nitrogen transport in surface nanocrystallized low-carbon steels during gaseous nitridation

J.F. Gu [a,b,*], D.H. Bei [a], J.S. Pan [a], J. Lu [b], K. Lu [c]

[a] *Key Laboratory for High Temperature Materials and Tests of the Educational Ministry, Shanghai Jiao Tong University, Shanghai, 200030, China*

[b] *LASMIS, University of Technology of Troyes, 10010 Troyes, France*

[c] *State Key Laboratory for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110015, China*

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Abstract

In the thermochemical process of low-carbon steel nitridation, improvements of mechanical properties are governed by the nature (hardness, thickness, etc.) of the compound layer since the compound layer will be kept under working conditions. Because of low nitrogen diffusivity in steel and low mass transfer between gaseous reaction and steel, long duration and high temperature are classically used for thermal nitridation. The present study shows that improved nitrogen transport can be obtained by gaseous nitridation after the samples have been surface nanocrystallized by ultrasonic shot peening (USSP). Comparing to the untreated samples, the nitridation efficiency of treated samples has been improved dramatically. The growth of γ' nitride layer conforms to a parabolic relationship with nitridation duration during the whole nitridation process in treated samples, while in untreated samples, the growth of nitride layer could be traditionally divided into two stages: the first linear growth stage and the second parabolic growth stage. This difference clearly indicated that the whole nitridation process is diffusion-controlled in treated samples instead of interface reaction-controlled stage and then diffusion-controlled stage in untreated samples. The high nitridation efficiency obtained may be explained by an increased volume fraction of grain boundary and an enhanced reactivity of surface atoms of the steel samples due to the nanostructure layer generated by surface nanocrystallization of USSP.

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Keywords: Gaseous nitridation; Growth; Reactivity; Diffusion; Nanostructure; Ultrasonic shot peening (USSP); Surface nanocrystallization

Steel nitridation is conventionally used in surface treatment to improve surface hardness, wear [1], fatigue [2] and corrosion resistance [3]. Because the nitrogen diffusion coefficient in steel is very small at low temperature, and is thermal-activated, gaseous nitridation is generally performed at the range of 500–600 °C. To ensure enough nitrogen diffusion length and the optimum nitrogen profile, gaseous nitridation will also need a considerable long duration. The long duration and high temperature classically used for thermal gaseous nitridation are the causes of undesirable deformation and structural modifications of starting materials, with expensive costs of manu-

* Corresponding author. LASMIS, Universite de Technologie de Troyes, 12 rue Marie Curie, BP 2060, 10010 Troyes Cedex, France. Tel.: +33-3-25-71-58-21; fax: +33-3-25-71-56-75.
E-mail address: jianfeng.gu@utt.fr (J.F. Gu).

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facture. To lower nitridation temperature and to improve nitridation speed as much as possible are always the great concerns of materials processing researchers all over the world [4,5]. The development of surface nanocrystallization process [6], which will generate a nanostructure layer on the surface of metallic materials without changing the chemical composition, provides a new solution. In this paper, we show the results of experiments performed on the surface nanocrystallized samples and untreated samples, which have shown significant improvements in gaseous nitridation.

The chemical composition (in weight percent) of the low-carbon steel 20# used in the study is listed in Table 1. First, the samples were prepared as a thin plate with a diameter of 20 mm and thickness of 3 mm for the ultrasonic shot peening (USSP) treatment. The principle of the USSP is based on the vibration of spherical shots using a high-power ultrasound. Because of the high frequency of the system, the entire surface of the component to be retreated is peened with a very high number of impacts over a short period of time. The main parameters of the USSP process were chosen as follows: the vibration frequency of the chamber driven by ultrasonic generator is 20 kHz, the shot diameter is 2 mm and the processing duration is 450 s. After USSP process, a layer with ultrafine-grained structure was observed by TEM on treated sample. The mean grain size at the top surface is approximately 10 nm and with a thickness of about 5 μm. Between the substrate and the nanostructure layer, a transition layer was observed in which the grain size gradually changed from nanometer to original size in the substrate material. The original grain size of untreated samples ranges from 10 to 15 μm. The related study results on USSP surface nanocrystallization technology and microstructure characterization of nanostructure layer have been reported in the published papers [6–8].

In the second step, the surface nanocrystallized samples and untreated samples were nitrided in a special tube nitridation furnace. There is a predissociation furnace for the ammonia to dissociate into reactive atomic nitrogen before it flows into the tube nitridation furnace. The nitrogen potential is controlled by the adjustment of the temperature of predissociation furnace, the ammonia flux and the gas pressure in the tube nitridation furnace. The nitridation treatments were carried out under three temperatures, 460, 500 and 560 °C, and the duration were 0.5, 3, 6, 9 and 18 h, respectively.

Table 1
Chemical composition of the low-carbon steel 20#

C	Mn	Ni	Cr	Mo	Al	Cu	Si
0.2	0.94	0.02	0.03	0.02	0.01	0.1	0.31

Table 2
Thickness of compound layer on different nitridation samples

Duration (h)	Thickness (μm)					
	460 °C		500 °C		560 °C	
	Treated	Untreated	Treated	Untreated	Treated	Untreated
0.5	0.5	1E − 4	0.75	0.1	2.5	1
3	1.75	0	3.125	1	7.5	2.5
6	2.5	0.25	4.5	1.5	10	5
9	3	0.5	5	2.5	12.5	6
18	5.25	2.5	6.25	3.125	15(ε)	8.125

The samples were oil-quenched after gaseous nitridation and the thickness of compound layers was measured by the metallographic observations. Table 2 shows the thickness of compound layer on different nitridation samples. The growth speed of surface nanocrystallized sample was obviously much quicker than that of untreated sample. Since it is the nitride layer formed during nitridation that improves the wear performance for short time nitridation of low-carbon steel, USSP surface nanocrystallization before nitridation can greatly shorten nitridation duration or decrease nitridation temperature and play an important role on the diminution of the deformation and on energy saving.

On most samples, the surface compound layers were totally consisted of γ′ -Fe_4N nitride and no ε-$Fe_{2-3}N$ nitride was observed except that on the treated samples' surface with 18-h gaseous nitridation treatment at 560 °C, a few ε-$Fe_{2-3}N$ particles in the surface were observed. This was confirmed by optical metallographic observations and X-ray diffraction analysis. Because it is easy to establish a simple and approximate mathematical model of γ′ -Fe_4N nitride layer growth [9,10], only the thickness of γ′ nitride will be discussed. Figs. 1–3 show the relationship between the thickness of γ′ and nitridation duration under three different temperatures. The growth of γ′ on surface nanocrystallized sample followed a para-

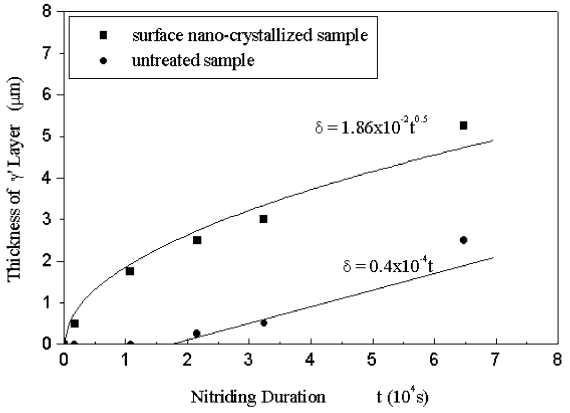

Fig. 1. Thickness of γ′ layer as function of nitridation duration at 460 °C.

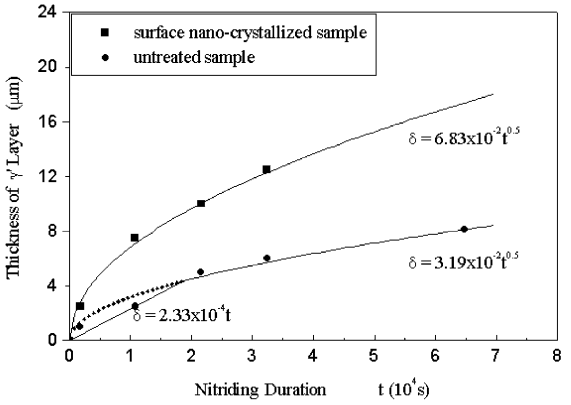

Fig. 3. Thickness of γ′ layer as function of nitridation duration at 560 °C.

bolic-like behavior characteristic of diffusion-limited kinetic: $\delta = At^{0.5}$. The coefficient A can be deduced by the model of γ′ growth and it has a linear direction proportion relationship with the nitrogen diffusion coefficient in γ′ phase, $A = \frac{C_3 - C_2}{C_2 - C_1} D_{\gamma'}^{N}$. Here, C_1 is solid solubility of nitrogen in α-Fe and C_2 and C_3 are upper and lower limit of nitrogen dissolved in γ′, respectively. For untreated samples, the growth of γ′ showed a linear relationship with nitridation duration at 460 °C and conformed to the parabolic rule well only in the latter stages of 500 and 560 °C nitridation. The value of coefficient A of surface nanocrystallized sample was almost twice that of untreated samples under all nitridation conditions. Therefore, we think that the reason that can explain the high nitridation rates is the improvement of nitrogen diffusion coefficient in nanostructure layer of surface-nanocrystallized sample.

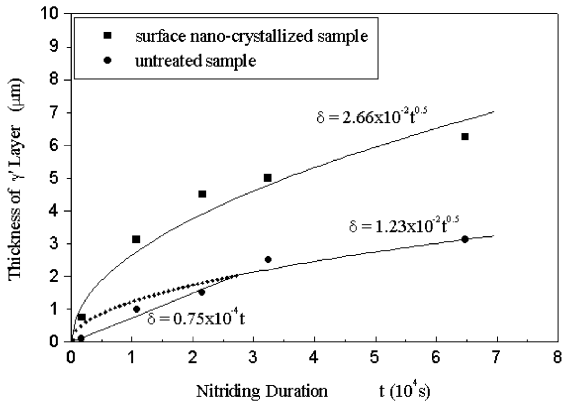

Fig. 2. Thickness of γ′ layer as function of nitridation duration at 500 °C.

It is more reasonable and traditional to divide the whole nitridation treatment of untreated samples into two stages as in the following table (see Figs. 1–3). The two-stage growth phenomenon can be easily explained [9,10]. It was shown from Table 3 that at 560 and 500 °C, the nitridation of untreated samples entered the second diffusion-controlled stage from the first interface reaction-controlled stage after about 5.2 and 7.5 h, respectively. At 460 °C, the continuous γ′ layer appeared on untreated samples after 6-h nitridation, and the nitridation was still in the first interface reaction-controlled stage after another 12-h nitridation. On the other hand, for the nitridation of surface nanocrystallized sample, another particularity is that the growth of γ′ conformed to the parabolic rule since the beginning of nitridation. The absence of the first

Table 3
Compound growth for untreated samples

Temperature (°C)	Duration (h)	Formula (δ (μm); t (s))
560	0–5.2	$\delta = 2.33 \times 10^{-4} t$
	5.2–18	$\delta = 3.19 \times 10^{-2} t^{0.5}$
500	0–7.5	$\delta = 0.75 \times 10^{-4} t$
	7.5–18	$\delta = 1.23 \times 10^{-2} t^{0.5}$
460	0–4.8	–
	4.8–18	$\delta = 0.4 \times 10^{-4} t$

interface reaction-controlled stage may explain that the USSP nanocrystallization treatment improved the reactivity of atoms in surface nanostructure layer [11] and then greatly speeded the interface reaction rate.

In conclusion, we have shown that the USSP process could increase significantly the diffusion and mass transfer of nitrogen during gaseous nitridation. The surface nanostructure layer generated by USSP plays an important role. The high diffusivity and reactivity of the atoms in this layer are the intrinsic reasons of the enhanced nitrogen efficiency. In order to obtain a better understanding of this enhanced nitrogen transport, a model of gaseous nitridation on surface nanocrystallized metals is under development to simulate the nitridation process. A series of further experiments such as nitridation under different parameters (temperature and duration) using the samples with different surface nanocrystallization conditions and microstructure/properties tests (hardness profile, nitrogen depth profile, TEM analysis, etc.) is in progress to determine the diffusion coefficient related to grain size and mass transfer coefficient between gas and metals.

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