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Gaseous nitriding behaviour of 33CrMoV12-9 steel: Evolution of the grain boundaries precipitation and influence on residual stress development

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ABSTRACT

The gaseous nitriding behaviour of 33CrMoV12-9 steel was investigated. The co-diffusion of nitrogen and carbon, precipitation at grain boundaries and mechanical properties evolutions (microhardness, residual stresses) are compared for several nitriding potentials, nitriding time and temperatures. While hardening unequivocally depends on the precipitation of alloying element nitrides MN (M = Cr, V…), the development of residual stresses follows phase transformation kinetics during nitriding. The transformation of carbides into nitrides is the limiting rate in the supersaturation of nitrogen in the ferritic matrix and the diffusion of the released carbon. The lower carbides transformation kinetics the smaller decarburization occurs during nitriding and residual stresses are more compressive. The kinetics is controlled by both the temperature and nitriding potential.

1. Introduction

Toughness of power transmission workpieces is well known to be enhanced by surface strengthening as well as compressive residual stresses [1]. Despite of industrial complications (e.g. process duration, atmosphere control…), gaseous nitriding of steels prevails over other surface treatments of steels by means of lower volumetric distortions of treated parts, higher surface completion and better microstructural (and mechanical) stability in service [2].

Gas nitriding of low alloyed steels consists in the diffusion of nitrogen atoms through the surface of a treated part [3]. Nitrogen is supplied by a surface catalytic decomposition of an ammonia-rich atmosphere at a temperature ranging from 450 to 590 °C. The nitrided case as obtained is usually characterized by a compound layer of iron nitrides $(\varepsilon)Fe_{2-3}N$ and/or $(\gamma')Fe_4N$ stretching up to 50 µm, and a diffusion zone where a dilute solute diffusion of nitrogen occurs in the ferritic matrix $(\alpha)Fe$.

In low alloyed steels, the diffusion layer is defined by the precipitation of fine alloying-element nitrides MN (M = Cr, V…) from the reaction of nitrogen with alloying elements either in solid solution in the ferritic matrix or within initial carbides $M_{23}C_6/M_7C_3$ from tempered martensite prior to nitriding [4–7]. Alloying-element nitrides are responsible of both surface strengthening as well as the generation of compressive residual stresses due to volumetric eigenstrains accompanying the precipitation [8–11]. Volumetric eigenstrains are a function of the specific volume of phases as well as changes in the lattice parameters due to chemical composition evolution of phases during nitriding and thermal expansion.

Cementite Fe_3C precipitation occurs at grain boundaries of prior austenite nearly parallel to the nitrided surface [12]. It lies in the carbon release within the ferritic matrix from the transformation of initial carbides into nitrides [5–7]. A co-diffusion of carbon has generally been observed during nitriding [5,13,14]. Depending on the nitriding potential, $K_N = P_{NH3}/P_{H2}{}^{3/2}$, the carbon atoms diffuse (i) toward the outer surface, leading to decarburization of the material or growth of a carbonitrides $(\varepsilon)Fe_{2-3}(N,C)$, and (ii) toward the nitrogen diffusion front, leading to an evolution of initial carbides [3,13,14].

While hardening is unequivocally related to the precipitation of fine alloying elements nitrides [2,4], the development of compressive residual stresses finds origins in the phase transformation kinetics [8–11]. It has been demonstrated to be influenced by the transformation of carbides into nitrides and the subsequent co-diffusion of carbon with nitrogen [5,14,15]. Some authors also referred to a creep phenomenon occurring during nitriding in order to explain the relaxation of residual stresses close to the extreme surface [16–18]. However, a lack of knowledge still exists on the transformation kinetics of carbides and its influence on the development of mechanical properties.

The present work aims investigating the nitriding behaviour of 33CrMoV12-9 steel grade. It focused on chemical and mechanical properties of the diffusion zone. The compound layer has generally

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been out of interest in industrial applications using the 33CrMoV12-9 steel grade. Carbon diffusion and grain boundaries precipitation were characterized using several nitriding parameters (time, temperature, nitriding potential) and emphasised with the subsequent mechanical response (hardness and residual stresses) of the nitrided cases was studied.

2. Materials and methods

2.1. Material preparation and nitriding treatment

The material of the present work is an industrial 33CrMoV12-9 steel grade. Rectangular samples of $17 \times 13 \times 5\,mm^3$ were austenitized at 950 °C during 30 min, oil quenched and annealed at 590 °C during 2.5 h. The ASTM grain size of prior austenite was controlled to 8–9 (15.9 to 22.5 μm). Prior to nitriding, specimens were machined on all sides, taken the grease out and finally cleaned using ultrasounds within ethanol.

Gaseous nitriding was performed in a SETSYS Evolution thermogravimetric analyser from Setaram Instrumentation (vertical alumina-made tube furnace and platinum-made suspension). The flow rate in the furnace was set to $200\,mL{\cdot}min^{-1}$. The nitriding atmosphere was composed of a gas mixture of NH_3-N_2-H_2. Mass-flow controllers adjusted the flow rate of each gas independently. Experimental conditions of gaseous nitriding were varied from 480 and 550 °C during 2.5 to 30 h (Table 1). According to the Lehrer diagram [19], two nitriding potential were set to 0.33 and $0.79\,atm^{-1/2}$ in the $(\gamma')Fe_4N$ domain and two others in the $(\varepsilon)Fe_{2-3}N$ domain (3.65 and $13.77\,atm^{-1/2}$). These conditions aim exploring nitrided cases with different kinks of compound layers.

2.2. Microstructure characterization

Cross sections of nitrided specimens were grinded and polished up to a 0.5 μm colloidal silica suspension. Observations were performed on a JEOL 7001F scanning electron microscope (SEM) operating at 15 kV and a current of 4 nA equipped with an Oxford Instrument INCA energy-dispersive X-ray detection system (EDX). The backscattered electron mode (BSE) was used for imaging due to a high Z contrast ratio between the matrix and phases at grain boundaries. The surface fraction of phases at grain boundaries was then determined by BSE-SEM image analysis. The surface was subdivided into 20 μm slices for in-depth profiling. Image analysis was performed using the ImageJ package [20]. Discrimination of phases at grain boundaries (cementite or iron nitrides) was made according to on one hand the Z contrast difference between cementite and iron nitrides, and on the other hand by EDX analysis. The procedure was used for qualitative estimation of the fraction of precipitates at grain boundaries and the error made by image analysis on BSE-SEM micrographs was not estimated in the present work.

Table 1
Experimental conditions for gaseous nitriding of 33CrMoV12-9 steel. The composition of the material at the gas-solid interface is given according to the Lehrer diagram [16].

Temperature [°C]	Time [h]	Nitriding potential [$atm^{-1/2}$]	Composition at the gas-solid interface
480	5	3.65	$(\varepsilon)Fe_{2-3}N$
	30		
520	5		
	30		
550	2.5		
	5		
	30		
	5	0.33	$(\gamma')Fe_4N$
	30		
	30	0.79	
	30	13.77	$(\varepsilon)Fe_{2-3}N$

2.3. Chemical analysis

Nitrogen and carbon contents were determined by optical emission spectrometry using a Spectro SPECTROMAXx MX5M BT. Four analyses were performed on four different areas without any overlapping on each nitrided surface. After each analysis, the size of area analysed is of nearly 0.5 mm diameter by 30 μm in depth. Depth profiling is obtained by successive mechanical grinding until elimination of previous sparks. Layer removal was controlled by dial indicator.

2.4. Mechanical characterization

The present work focused on mechanical properties of the diffusion zone defined by a ferritic matrix α-Fe. This is the reason why in-depth profiles start at 50 μm below the outer surface.

Hardness was obtained using a Leica VMHT device with a load of 2 N during 15 s. The effective depth of nitriding is defined as the core hardness plus 100 HV 0.2.

X-ray analysis was carried out on a Siemens D500 diffractometer equipped with a linear detector and Cr-K_α radiation (giving a penetration depth of approximately 6.5 μm). Residual stress analyses were performed on the {211} diffracting plane of α-Fe. The $\sin^2\psi$ method was used to determine the mean residual stresses $(\sigma_{xx} - \sigma_{zz})$ in α-Fe along the nitriding depth z [21]. X-ray elastic constants were calculated from α-Fe elastic constants using a Kröner-Eshelby model ($S_1{}^{\{211\}} = -1.25.\ 10^{-6}\ MPa^{-1}$; $\frac{1}{2}S_2^{\{211\}} = 5.85.\ 10^{-6}\,MPa^{-1}$) [22]. Electro-chemical surface layer removal (controlled by dial indicator) was carried out using a Struers Lectropol 5 device for in-depth profiling. Residual stress profiles were finally corrected from successive layer removal using the modified Moore and Evans approach [23,24].

3. Results

3.1. Microstructure

3.1.1. The compound layers

The first 75 μm of the nitrided cases were observed by scanning electron microscopy. The backscattered electron mode (BSE) was used in order to distinguish iron carbides from iron nitrides at grain boundaries of prior austenite grains. According to the atomic numbers of elements and composition of iron nitrides ($(\varepsilon)Fe_{2-3}N$ and $(\gamma')Fe_4N$) and carbides (Fe_3C cementite), nitrides bring out darker than carbides on SEM-BSE micrographs. EDX mapping was also used to confirm observations (Fig. 0).

Depending on the nitriding potential, different kinds of nitrided surfaces are observed at 550 °C (Figs. 1 and 2). At $0.33\,atm^{-1/2}$, no compound layer is present except after 5 h of nitriding where $(\gamma')Fe_4N$ nucleated on several areas. When increasing the nitriding potential, a compound layer developed and is composed of iron nitrides $(\varepsilon)Fe_{2-3}N$ and $(\gamma')Fe_4N$ as confirmed by XRD analysis (Figs. 3 and 4). The higher nitriding potential, the thicker the compound layer is.

For a given nitriding potential of $3.65\,atm^{-1/2}$, a compound layer systematically developed between 480 and 550 °C. The higher temperature the thicker the compound layer is (Figs. 5 and 6). After 30 h of nitriding, the precipitation of iron nitrides from grain boundaries and prior martensite laths is less pronounced when the temperature increases (Fig. 6). The compound layers are characterized by iron nitrides $(\varepsilon)Fe_{2-3}$ N and $(\gamma')Fe_4N$ as confirmed by XRD analysis (Figs. 7 and 8).

The nitrides surfaces are characterized by a thin porous and brittle layer at the outer surface composed of mainly $(\varepsilon)Fe_{2-3}N$. The thickness of this layer increases when nitriding parameters increase, i.e. when the nitrogen content is closed to equilibrium with the NH_3-rich atmosphere (recombination of N as N_2 [2]).