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Acta Materialia 61 (2013) 3963–3972

Acta MATERIALIA

www.elsevier.com/locate/actamat

Phase transformations in the nitrocarburizing surface of carbon steels revisited by microstructure and property characterizations

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Received 4 January 2013; received in revised form 18 February 2013; accepted 24 February 2013
Available online 25 April 2013

Abstract

Ferritic nitrocarburizing is a widely employed industry process by which a strengthened nitrocarburized surface can be formed on mechanical tools or parts made of steels. Mainly composed of the ε-$Fe_{2-3}(C,N)$ and γ′-$Fe_4(C,N)$ carbonitride phases as well as the α-Fe phase, the nitrocarburized surface has featured microstructures and properties that are directly related to the phase transformations occurring in the surface layers. Thus far, the following phase transformation sequence for the surface has generally been accepted: α-Fe + N/C → ε → γ′. In the present work, these phase transformations were systematically revisited by microstructure and property characterizations in association with a controlled nitrocarburizing process by which the microstructures and properties of the surface are adjustable. Our study demonstrates that, to fully understand the microstructure and the property of a nitrocarburized surface, it is necessary to adopt the phase transformation sequence α-Fe + N/C → γ-N/C + N/C → γ′ + N/C → ε, in which the existence of a transitional austenite phase containing N/C atoms (γ-N/C) must be assumed and the γ′ phase actually forms prior to the ε phase.

Keywords: Nitrocarburizing; Phase transformation; Carbonitrides; Electron microscopy; Multiple twins

1. Introduction

Ferritic nitrocarburizing, being a thermal chemical surface treatment process at a temperature below 592 °C (the eutectoid temperature of the Fe–N alloy system), has been widely used to improve the surface properties, such as corrosion resistance, wear resistance and fatigue resistance, of mechanical tools and parts made of iron alloys and steels [1–10]. The nitrocarburized surface of carbon steels usually consists of an outermost compound layer and an inner diffusion layer. In some cases a transition layer may be formed between the above two layers [6,9]. Usually, the compound layer is composed of both the ε-$Fe_{2-3}(C,N)$ and γ′-$Fe_4(C,N)$ carbonitrides, though the θ-Fe_3C cementite phase may appear in a specially designed low-N/C-ratio nitrocarburizing process [11–13]. It is often observed that the compound layer can be further divided into an upmost ε carbonitride sublayer and an inner γ′ carbonitride sublayer [6,9,14–16]. The properties of such a nitrocarburized surface are strongly dependent on the microstructures formed, including the carbonitride phases and the thicknesses of these (sub)layers, whereas the microstructures are directly related to the phase transformations that occur in these layers. Hence understanding these phase transformations is particularly important for the improvement of the nitrocarburizing process.

It has been shown that the phase transformations occurring in the nitrocarburized steel surface are governed by the nitrocarburizing parameters, such as the temperature, gas composition and cooling path (or method) [6,9,14–16]. The currently accepted phase transformation sequence in the nitrocarburized steel surface originated from the iron nitride formation mechanism proposed in 1965 by Kölbel

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1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2013.02.058

et al. [17], who suggested that in a plasma nitriding process the formation of iron nitrides follows the reaction path: α-Fe + N → FeN → Fe_2N → Fe_3N → Fe_4N. This nitriding mechanism has been supported by the studies of several other researchers [18–23], and since then has become the generally accepted formation mechanism of the nitride/carbonitride phases in the nitrocarburized layers of carbon steels in the following form [6,14–16]: α-Fe + N/C → ε-$Fe_{2–3}(C,N)$ → γ'-$Fe_4(C,N)$. This mechanism infers that, in the nitrocarburized layers that include a compound layer, a diffusion layer and a transition layer (if appeared), the ε phase is first precipitated from the ferritic α-Fe matrix containing supersaturated N/C atoms and then the ε phase transforms into the γ' phase through a decomposition mechanism. The portion of the ε phase grains (or sublayer) with respect to the portion of the γ' phase grains (or sublayer) may vary in different cooling processes [15,16]. Nonetheless, Somers and Mittemeijer [24] argued that the dissolution and diffusion of nitrogen into the ferrite substrate governs the formation and growth kinetics of iron nitrides, and they believed that the γ' phase first nucleates at the surface and then the ε-nitrides nucleate on the γ'-nitrides, though their supporting experimental data were very limited. Hence the formation mechanism of the carbonitride phases is still a somewhat controversial issue in the understanding of a nitriding/nitrocarburizing process.

In fact, current understandings of the phase transformations and the relations between the phases formed in a nitriding/nitrocarburizing process become even more controversial and ambiguous if more individual results published in the literature are examined with regard to this same issue. This is partly due to the fact that the problems involved have not been well defined, partly due to the complexity of the phase transformations that occur during the process, and partly due to the fact that the characterization methods used in the studies are not sufficiently accurate or comprehensive, as analyzed below.

First, the phase transformations occurring in a ferritic nitriding/nitrocarburizing process actually belong to two classes: those transformations that occur in the nitrocarburizing stage at the highest temperature of the process and those that occur in the cooling stage down to room temperature. However, the phases formed in these two different stages are mixed up in the final microstructures and have never been distinguished clearly. For example, both the phase diagram of the Fe–N alloy system [25] and first-principles energy calculations [26,27] indicate that at a ferritic nitriding temperature (below 650 °C) the γ' phase is the stable one in those parts of the Fe-matrix where the N concentration is less than 20 at.%, whereas the ε phase is more stable in those places where the N concentration is beyond 26 at.% (the two phases can coexist where the N concentration is in the range of 20–26 at.%). Theoretically, at the beginning of the process, the N concentration should be low in the Fe-matrix and the γ'-particles would form first. These γ'-particles would then quickly transform into ε-particles in the outer surface area, where the N concentration can rapidly increase beyond 20 at.%. However, these transformations are difficult to monitor experimentally. On the other hand, it has been clearly shown, via a slow cooling process [6,20] and an annealing process [16,21], that the low-nitrogen ε-nitrides transform into the γ' phase as the N atoms they contain diffuse into the matrix.

Secondly, as well as the α-Fe-matrix phase, the γ' phase and the ε phase, an austenite phase containing nitrogen (referred to as γ-N/C) may form during a ferritic nitrocarburizing process, as shown by Mössbauer measurements [9,28,29]. This implies that the phase transformations involved in a nitrocarburizing process could have been much more complex than what have thus far been understood or reported in the literature. Nonetheless, since the amount of retained austenite detected by Mössbauer measurements is too small to be observed by other characterization tools, stronger evidence is needed to confirm the formation of the γ-N/C phase at ferritic nitrocarburizing temperature, which is below 592 °C, i.e. the eutectoid temperature of Fe–N alloys. Theoretically, if a ferritic nitrocarburizing temperature of around 565 °C is chosen, as is usually done in practice, the γ-N/C phase can form in those parts of the Fe-matrix with the right N/C concentration, since the eutectoid temperature of the Fe–C–N alloy system is lowered to 565 °C [25]. Thus, using the conventional definition of a ferritic nitrocarburizing process with respect to the eutectoid temperature of Fe–N alloys (592 °C) to try to understand the possible phase transformations that occur in the process is actually somewhat misleading, as it excludes the γ-N/C phase.

Thirdly, in the studies of the microstructures of nitrocarburized layers, optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been widely employed, whereas transmission electron microscopy (TEM) has been used comparatively less. However, as analyzed above, fine microstructure details may exist and could provide crucial information about the complex phase transformations occurring in the nitrocarburization processes. More TEM examinations are therefore needed to reveal the fine microstructures of the nitrocarburized layers. Furthermore, consistent with the demand for fine microstructure characterization, both the macroproperties and the microproperties should be characterized, in order to understand the detailed contributions of each individual layer to the macroproperties of the nitrocarburized surfaces of steels.

In the present work, it is demonstrated that, in a nitrocarburizing process of carbon steel, the thickness of the transition layer between the compound layer and the diffusion layer is controllable, ranging from 0 to 20 μm, by changing the C/N concentration ratio in the nitrocarburizing gases. Detailed microstructure and property characterizations of the transition layers consistently reveal that the γ-N/C phase had been formed at a nitrocarburizing temperature between 560 and 580 °C. Both experimental evidence and first-principles energy calculations indicate that the phase transformation sequence occurring during a