Applied Surface Science 271 (2013) 156–163

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Microstructural evolution during nitriding, finite element simulation and experimental assessment

S.M. Hassani-Gangaraj, M. Guagliano*

Politecnico di Milano, Dipartimento di Meccanica, Via La Masa, 1, 20156 Milano, Italy

ARTICLE INFO

Article history:
Received 27 October 2012
Received in revised form 21 January 2013
Accepted 22 January 2013
Available online 29 January 2013

Keywords:
Nitriding
Finite element simulation
Microstructure
Layers growth kinetics
Nitrogen distribution
Mechanical characteristics

ABSTRACT

A finite element simulation of nitriding is proposed in this paper, using the analogy between diffusion and heat conduction, to overcome the shortcomings of the classical internal oxidation model in predicting the kinetics of layer growth and nitrogen distribution during nitriding. To verify the model, a typical gas nitriding has been carried out on an axisymmetric specimen. Treated specimen has been characterized using optical microscopy (OM), scanning electron microscopy (SEM), micro-hardness and X-Ray diffraction (XRD) measurements. It was found that the so-called diffusion zone can be divided into two parts with different influence on the mechanical characteristics including residual stress and hardening. First layer which is a two phase region of ferritic matrix and γ' (Fe_4N) makes further improvement with respect to the second layer which is a solid solution of nitrogen in ferrite. The formation of that two phase region, which is not predicted by classical model, can be efficiently recognized by the proposed model. It is also proved that the model has the ability to consider the geometry dependency of layer growth and formation in nitriding.

1. Introduction

Gas nitriding is a case hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature (below Ac_1, for ferritic steel) in contact with nitrogenous gas, usually ammonia [1]. At the conventional nitriding temperature, 495–565 °C for steels, ammonia is an unstable thermodynamic state and decomposes to nitrogen and hydrogen. The released nitrogen atoms have the opportunity to either chemically react with or diffuse between iron atoms. Formation of iron nitrides on the immediate surface results in the so-called compound or white layer. The composition of this hard and brittle layer is dependent on nitriding potential and temperature. However, with the conventional processing parameters it is usually a combination of γ' (Fe_4N) and ε ($Fe_{2-3}N$) phases. Beneath the compound layer, nascent nitrogen atoms interstitially diffuse into octahedral interstices of BCC structured iron and the so called diffusion zone is formed. Precipitation of alloying elements after combination with nitrogen can also take place in the diffusion zone.

From a practical point of view, gas nitriding does not require a phase change from ferrite to austenite [2]. Therefore, it can be conducted at a relatively lower temperature as compared to other hardening methods. From a mathematical point of view, nitriding can be regarded as a diffusion phenomenon in which material transfer occurs as a result of random molecular motion. More than five decades Wagner's classical internal oxidation model [3] was the foundation of reactive diffusion kinematics research in solid materials. Somers and Mittemeijer [4], Trochane et al. [5] and Du et al. [6] have applied this classical model to predict the nitrogen transfer rate in solid, the nitride layer growth rate, and the nitrogen concentration profiles during gas nitriding of iron. Their approach is based on the formation of sharp boundaries in which precipitation occurs, the parabolic law of growth and error function type distribution of concentration [7]. The approach afterwards has been used several times in the literature to calculate layer growth during gas or plasma nitriding of iron or steel [8–12]. However, shortcomings and simplifying assumptions behind it should not be overlooked. These include:

(i) Despite of its wide acceptance and application, nitrogen concentration calculated by this method has not yet been verified in whole compound and diffusion zone. In its early application, Somers and Mittemeijer [4] presented a comparison of calculated concentration with the measured profile by electron probe micro-analyzer (EPMA) up to 12 μm in depth. Du et al. [6] reported the concentration distribution of nitrogen up to 15 μm in depth. It should be reminded that in a typical nitriding process, the hardened case depth is usually in the order of several hundred micrometers and the compound layer depth is within 0–20 μm. Seeing in this light, it can be concluded that there is a lack of verification of nitrogen concentration

* Corresponding author. Tel.: +39 02 23998206; fax: +39 02 23998202.
E-mail addresses: mario.guagliano@polimi.it, mario.guagliano@gmail.com (M. Guagliano).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.01.154

profile in whole diffusion zone. Most recently, Hosseini et al. [13,14] characterized nitrogen concentration depth profiles in the compound layer and the diffusion zone by several techniques including energy dispersive spectroscopy (EDS), glow discharge optical emission spectroscopy (GDOES) and secondary ion mass spectrometry (SIMS). They found that, there are major differences between EDS and GDOES with SIMS profiles at the inner section. In EDS and GDOES profiles nitrogen concentration was decreased to nearly zero very close to the nitrided surface, while SIMS profiles show a very smooth gradient down to several hundreds of micrometers. They explained that elements concentration must be sufficiently high to be detected by EDS and GDOES. As the concentration of nitrogen decreased in diffusion zone, it is not within the sensitivity of both EDS and GDOES. Accordingly, diffusion depth cannot be measured accurately. GDOES has been most often applied in the literature [15–17] to quantify nitrogen concentration. This method shows very accurate data within the compound layer while it is not able to reflect an accurate nitrogen depth profile in the diffusion zone [14]. Accordingly, it can be concluded that the precision of application of the classical internal oxidation model below the compound layer has not yet been affirmed.

(ii) According to the classical internal oxidation model applied for nitriding, diffusion zone is constituted by a single phase α in which nitrogen atoms diffuse interstitially. This assumption is in an inconsistency with microstructural examinations of nitrided layers by optical microscopy (OM) and scanning electron microscopy (SEM) observation reported in the literature [13,14,16,18–21]. The common feature of all these observations is that γ' precipitated in ferritic matrix and formed a needle shape phase. Beneath the compact layer on the surface which is combination of ε and γ', ferritic matrix does not appear quickly. Instead, a two phase region of $\alpha + \gamma'$ is formed between compound layer and ferritic matrix. This observation is strongly supported by Fe–N phase diagram [2]. At a common nitriding temperature, a wide range of concentration lies in the two phase region of $\alpha + \gamma'$. Presence of this region that has been proved by microstructural assessment and supported by phase diagram is completely ignored by the internal oxidation model applied for nitriding.

(iii) The analytical solution in the form of error function distribution and parabolic law of growth, applied to nitriding, is exact if the surface concentration remains constant during diffusion and the considered body is semi-infinite. In fact, this analytical distribution originated from the Neumann solution of the classical Stefan problem [22]. In mathematics and its applications, particularly to phase transitions in matter, a Stefan problem is a particular kind of boundary value problem, adapted to the case in which a phase boundary can move with time. The classical Stefan problem aims to describe the temperature distribution in a homogeneous medium undergoing a phase change, for example ice passing to water. Exact solution of the classical Stefan problem exists under the above-mentioned conditions. Rozendaal et al. [23] measured the amount of surface nitrogen concentration in different processing times of gas nitriding and showed that surface concentration is not constant during this process. Violation of the parabolic law of growth for both compound and diffusion layers has been also reported in the literature [8,18]. These observations indicate that the conditions of exact analytical Neumann solution of the classical Stefan problem may not be met in the nitriding process. In addition, the geometry dependency of nitrogen concentration, microstructure of nitrided surface layers and resultant hardness has been experimentally approved [15,24,25]. In another word, the distribution of concentration for a semi-infinite body would not be able to assess the circumstances occurring in more complicated geometries like grooves, notches, curved surfaces, inner and outer corners which are typically being subjected to nitriding.

Despite the importance and wide application of nitriding, a deep knowledge of the case depth, nitrogen concentration distribution and their dependency on relating parameters are still lacking. For nearly two decades classical internal oxidation model has been widely applied to predict the kinetics of layer growth and nitrogen distribution during nitriding. Nonetheless, it was mentioned that this model suffers from some serious shortcomings. To overcome the aforementioned shortcomings, a finite element simulation of nitriding is proposed in the present study. The capability of finite element model to simulate different layer's growth including phase change is verified by analytical solution. Afterward, a finite element technique is proposed to simulate a nitriding process using the analogy between diffusion and conduction heat transfer. To assess the accuracy of the results, a typical gas nitriding process has been carried out on an axisymmetric specimen. Treated specimen has been characterized using OM, SEM, micro-hardness and X-Ray diffraction (XRD) measurements. Comparing experimental observation with finite element prediction, a critical discussion is presented on the microstructure and layer growth of nitrided specimen.

2. Diffusion-heat conduction analogy

If the mathematical formulation of solidification process (classical Stefan problem) in a semi-infinite region, energy balance in solid/liquid interface and its analytical Neumman solution [22,26] is compared with the formulation of a diffusion problem in a simple eutectic system with limited solubility on each side, the mass balance at the interface [27] and the applicability of Neumman's particular solution to express the concentration profile [7], a straightforward analogy between governing equations of diffusion and heat conduction can be realized. Regarding the boundary condition, proposed relation by Rozendaal et al. [23], taking the variation of surface concentration into account by introducing the reaction rate coefficient, is corresponded to the well-known convection boundary condition in heat transfer.

To the best of author's knowledge, commercial finite element packages either do not have a special scheme for simulation of diffusion or their scheme has not yet been well developed to consider the effect of moving boundaries or non-constant surface concentration. At the same time they have a powerful scheme for simulation of heat transfer phenomena. By this promising analogy between diffusion and heat conduction, finite element simulation of gas nitriding would be also possible. The significance of finite element simulation over analytical solution lies in its ability to accommodate more accurate boundary conditions and more complex geometries with less simplifying assumptions bearing in mind that an exact analytical solution of the Stefan problem even in the one-dimensional case is possible only in a few simple cases. Implementation of this analogy will be more clarified in Section 5.

3. Validation of finite element simulation

Before using heat conduction and diffusion analogy to simulate nitriding, the accuracy of finite element model in evaluation of interface formation and its growth in a two phase problem is verified in this section by simulation of a solidification problem and comparing the result with the well-known analytical Neumman solution [26]. A liquid having a phase change temperature is confined to a semi-infinite region. Initially, it is at a uniform temperature which is higher than phase change