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Compositional depth profile investigation of plasma nitriding by multiple analyses techniques

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ABSTRACT

Compositional depth profile in plasma nitriding is investigated by several experimental techniques including EDS, GDOES and SIMS as well as a calculated method. Plasma nitriding was carried out on high purity iron substrate at a temperature of 550 °C in an atmosphere of 75 vol.% H_2–25 vol.% N_2 for time periods of 1, 2, 5 and 10 h. SEM and XRD methods were used for microstructural evaluation and phase identification. According to EDS, GDOES and calculated data, composition of the compound layer reached nearly to Fe-8 wt% N and Fe-6 wt% N indicating ϵ-$Fe_{2-3}N$ and γ′-Fe_4N nitrides were formed, respectively. Although nitrogen concentration was decreased to nearly zero close to the nitrided surface, calculated data and SIMS profiles show very smooth gradient in diffusion zone down to several hundreds of micrometers. The results of compositional depth profiling by EDS, GDOES and SIMS indicated good agreement between experimental findings and, thus, the techniques completed one another. It was found that EDS and GDOES are appropriate for analysis of Fe and N in the compound layer, but both have limitations for profiling of nitrogen in the diffusion zone. SIMS, on the other hand, was distinguished as a professional technique for accurate measurement of nitrogen within the diffusion zone. The experimental depth profiles indicated good consistency with calculated diffusion profiles for all treatment cycles.

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1. Introduction

Concentration depth profiling of nitrogen in plasma nitrided surfaces can be considered as a quality control approach to predict the properties of the treated components. Measurement and depth profiling of the light elements (mainly nitrogen) in nitrided substrates which have a relatively high Z matrix (mainly Fe) is still not fully elucidated [1]. Nitrogen is a light element with a relatively low concentration in plasma nitrided components and, thus, there are difficulties for its accurate measurement if only one of the conventional surface analysis techniques is employed. Normally, energy dispersive spectroscopy (EDS) is used for detecting the diffused elements in surface layers, but there are limitations for accurate measurement of nitrogen in nitrided components. Glow discharge optical emission spectroscopy (GDOES) as a powerful and versatile analytical technique has been used successfully for concentration depth profiling of substitutional atoms in binary Ti–Cu and quaternary Ti–Cu–Al–V diffusion systems [2–4]. Nevertheless, the difficulties and limitations, even with GDOES, are major for profiling of nitrogen in diffusion zone, in comparison with compound layer, because of lower nitrogen concentration and deeper diffusion depth. Although many research works have been conducted for detecting nitrogen in diffusion treated parts, there still remain major problems for accurate measurement and profiling of nitrogen concentration in nitrided components.

Mittemeijer and Somers investigated growth and control parameters of gas nitriding process of pure iron and reported a nitrogen depth profile of 100 μm [5,6]. They used EPMA for detection of nitrogen in compound layer, but no exact experimental data have been reported for diffusion zone. Du et al. studied gaseous nitriding and nitrocarburising of iron specimens by light microscopy, XRD and EPMA [7,8]. Concentration depth profiles of nitrogen and carbon, reported by them, were limited to compound layer, i.e. up to 15 μm depth from the surface.

Sun and Bell investigated on computer prediction of threshold nitriding potential curves and introduced a numerical model of plasma nitriding process [9,10]. They developed a mathematical model to simulate the plasma nitriding process, considering the simultaneous diffusion of nitrogen in ferrite, precipitation of nitrides in the diffusion zone and development of γ′-Fe_4N iron nitride layer

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on the surface. They calculated concentration depth profile of pure iron during plasma nitriding at 560 °C in $6N_2$–$94H_2$ mixture for nitriding periods from 0.2 to 1.2 h. With increasing nitriding time, the nitrogen profile gradually moved upward and the surface nitrogen concentration gradually approached the equilibrium value.

Malaczynski et al. analyzed pure iron surfaces modified by plasma immersion ion implantation and conventional plasma nitriding using XPS [11]. Although they detected nitrogen concentration in compound layer quantitatively, their results did not show the depth of the nitrogen diffusion; instead, the horizontal axis is the sputtering time. As they mentioned a sputtering rate of 9.2 nm/min and duration of 2000 s, the maximum detected depth of nitrogen would be 0.31 μm.

Yan et al. simulated nitrogen distribution during pulse plasma nitriding of pure iron at 520 °C for different nitriding times [12]. They measured nitrogen concentration profiles in the compound and diffusion layers, as well as the diffusion depth by GDS, an ion probe technique and optical microscope, respectively. Their experimental depth profiles had only five points in diffusion zone, less than 0.1wt% N, and could not be figured out quantitatively. Multiple techniques have been used by Gontijo et al. who characterized plasma nitrided pure iron by SEM, EDS, XRD and XPS for semi-quantitative analysis [13]. The Rietveld analysis was performed to investigate the concentration variations of the phases as a function of nitriding time. However, they did not report any concentration depth profile in diffusion zone.

Kamminga and Janssen calculated nitrogen depth profiles in nitrided ferritic steel on the basis of precipitation and trapping models [14]. A discrepancy existed between experimental nitrogen depth profiles, from literature, and precipitation model calculations. Experimental data agreed with nitrogen depth profiles calculated with the trapping model, but it showed that the trapping model was too simple for accurate determination of nitrogen diffusion during nitriding. Keddam simulated the pulse plasma nitriding process of pure iron using a kinetic model derived from the Fick's laws [15]. They compared a few experimental data from literature with their theoretical results and showed the reliability of the model in compound layer but, for the diffusion zone, no depth profile was presented.

Hirsch et al. used XRD analysis to investigate growing nitride layers during plasma nitriding under two gas mixtures [16]. Depth profile analyses performed by GDOES technique revealed the nitrogen to a depth of about 25 μm from the surface, indicating compound layer and transition zone, but no profile was reported for maximum depth of the diffusion zone.

Analytical calculation based on error function approach has been used previously for most of the diffusion problems, including nitriding process [7,12,15,17–20]. Based on this approach, the present authors presented primary and simple analytical solutions for 'nitrogen distribution' and 'compound layer growth' during nitriding of pure iron [21,22]. Calculation of nitrogen diffusion based on Fick's laws revealed that nitrogen diffused in iron to depths of several hundreds of micrometers in such concentrations that could not be detected by conventional procedures. Nitrogen depth profile of diffusion zone in plasma nitrided pure iron was analytically calculated and experimentally measured by optical and scanning electron microscopy and indicated good agreement with calculated diffusion depths [23]. Diffusion of the nitrogen in both, the compound layer and the diffusion zone, were characterized by optical and scanning electron microscopy as well as the SIMS technique [24]. Diffusion of nitrogen in plasma nitrided iron and structure evolution during the nitriding process were studied by optical microscopy, microhardness depth profiling, scanning electron microscopy and X-ray diffraction [25]. From this research, case depth, thickness of the compound layer, nitrogen depth profile and

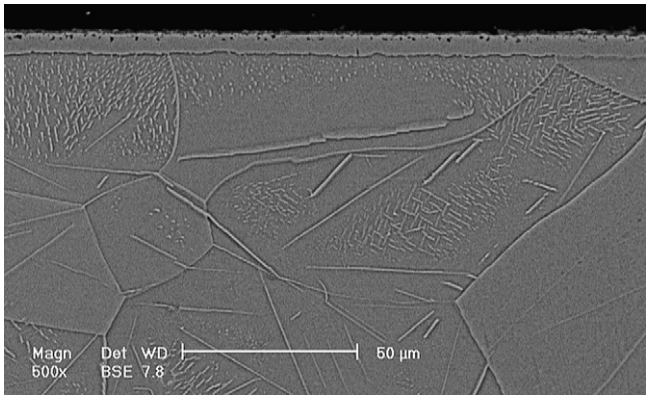

Fig. 1. A typical scanning electron microscopy (SEM) from cross section of plasma nitrided sample (2 h at 550 °C).

characteristics of intermediate nitrides including ε, γ′ and $Fe_{16}N_2$ were determined. Recently, the primary and simple models [21,22] were improved and 'nitrogen concentration depth profile' as well as 'thickness of compound layers' in the nitriding process of pure iron were modeled more accurately [26,27]. The results of modeling were compared with the experimental data in the gaseous and plasma nitriding process and a good agreement was confirmed.

The present paper is concentrated on depth profile investigation in plasma nitrided iron by various analyses methods. Several techniques including energy dispersive spectroscopy (EDS), glow discharge optical emission spectroscopy (GDOES) and secondary ion mass spectrometry (SIMS) were used consecutively for evaluation of the elements diffused in both 'the compound layer' and 'the diffusion zone' from the surface through the depth of the substrate. The results of experimental measurements are compared and contrasted with depth profiles calculated based on the improved analytical models presented by previous authors.

2. Materials and methods

2.1. Substrate and treatments

Disc-shaped ARMCO iron samples, 25 mm diameter and 5 mm thickness, were prepared from 30 mm diameter bars. Chemical composition and impurity levels of the substrate material as well as

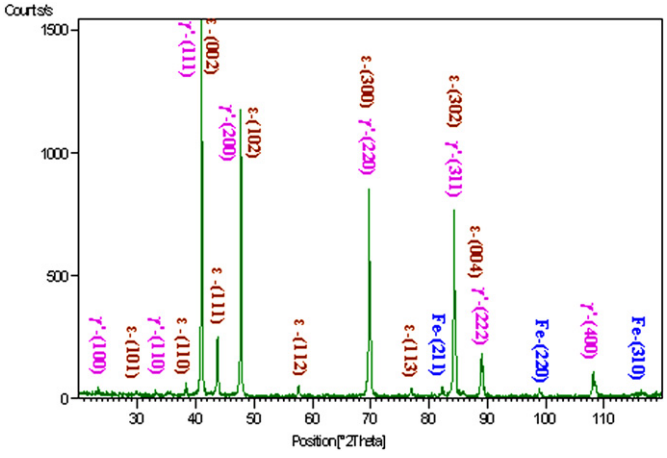

Fig. 2. X-ray diffraction (XRD) pattern of plasma nitrided sample (2 h at 550 °C).

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