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Combination of mechanical and chemical pre-treatments to improve nitriding efficiency on pure iron

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ABSTRACT

In this paper, the efficiency of gas nitriding on pure iron is observed regarding two types of pre-treatments prior to nitriding: chemical reduction by H_2 and nanocrystallization by NanoPeening®. Thermogravimetric analysis reveals that both pre-treatments result in an increase in the transformation rate of nitrogen during the first 200 min of nitriding. Moreover, glow discharge optical spectrometry reveals that nanocrystallization by NanoPeening® leads to a deeper penetration of nitrogen in the material.

1. Introduction

Manufacturing surface having high near-surface mechanical properties (hardness, compressive residual stresses) is one of the major challenges for increasing the lifetime of mechanical parts. Surface mechanical treatments like shot peening, or thermochemical techniques like nitriding, lead to compressive residual stresses [1] which prevent the initiation of cracks. To face abrasive and adhesive wear, it is well known that hardness has to be maximized. One way to obtain higher near-surface mechanical properties without changing materials composition is to use surface mechanical treatments, which can induce grain fragmentation resulting in ultrafine grains or nano-sized grains [2–4]. This leads naturally to an increase in hardness and yield stress thanks to the well-known Hall–Petch effects [5,6] as shown by Tumbajoy-Spinel et al. [7].

Such nanocrystallization treatments offer one other significant advantage: the enhancement of diffusion phenomena thanks to the increase in grain boundaries density. As shown by Tong et al., the surface mechanical attrition treatment (SMAT) leads to deep penetration of nitrogen upon nitriding at 300 °C of an austenitic stainless steel. Let us highlight the fact that nitriding of such materials at such a temperature is usually inefficient on non-mechanically treated samples. Gu et al. [8] observed on a low carbon steel, that SMAT prior to nitriding improves the thickness of the nitrided layer. Moszynski et al. [9] studied the nature of nitride phases formed during nitriding on nanocrystalline iron and showed that nanocrystallization induces the stability of iron-nitrogen phases that cannot be observed with coarse grain material. They also showed that the compound layer formation requires a lower nitriding potential than in the case of coarse grain material [10]. The penetration depth of nitrogen was observed to be double compared to nitriding used alone. Lin et al. [11], Tong et al. [12] and Prezeau et al. [13], also showed on different steel grades (respectively AISI 321, 38CrMoAl, AISI 304L, 32CrMoV13 and X37CrMoV5-1) that surface nanocrystallization prior to nitriding increases the hardness after treatment. Terres et al. [14] showed on 42CrMo4 steel that the compressive residual stresses obtained by shot peening can be combined to those obtained by nitriding, leading to an improvement of the fatigue resistance.

Nevertheless it is apparent, that the benefits of associating these two treatments are sometimes a matter of debate. For instance, the increase in fatigue resistance is not observed by Hassani et al. [15] who investigated the combination of nanostructuration by severe shot peening and nitriding on 32CrMoV13 steel. However,

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they highlighted that for equivalent output properties (hardness, fatigue limit and residual stresses), the nitriding duration on a 35NiCrMoV12-5 steel can be reduced by applying a nanocrystallization pre-treatment [16]. Manfridini et al. [17] also observed on Ti-stabilized interstitial-free steels that the combination of such treatments does not improve mechanical properties compared to single treatments, but no information about the gain in nitriding duration is given. Chemki et al. [18] showed on austenitic steels that the nitriding efficiency could be further improved if SMAT was followed by a slight polishing step, pointing out that nanocrystallized layers can sometimes be accompanied by side effects (e.g. surface oxidation) that play a detrimental role on diffusion.

In practical conditions, oxide layers can act as a barrier to the diffusion of nitrogen. Thus, it is well known that a chemical cleaning by reduction of oxides improves the efficiency of nitriding [19,20]. For example, De Las Heras et al. [21] prepared their samples by heating them in a 50/50 Ar/H_2 mixture for 3 h before nitriding. Jones [22] observed an increase in the hardness on AISI 4140 steel after nitriding when samples where initially pre-oxidized and reduced during nitriding.

Most of investigations about the combination of nitriding with mechanical pretreatments are based on post-mortem mechanical and microstructural characterization. Only a few of them address the consequences of such pre-treatments on nitriding kinetics. This is the aim of the present paper. For that purpose an extensive analysis of the nitriding kinetics is performed using thermogravimetric analysis and glow discharge optical emission spectroscopy to obtain an in-depth nitrogen profile after nitriding. These investigations are conducted on pure iron samples, chosen as model material, which are successively submitted to two types of surface pre-treatments before nitriding:

- Surface nanocrystallization by NanoPeening® [4];
- Chemical surface preparation by reduction.

The effects of each pre-treatment and their combination on the nitriding kinetics are carefully examined, which has never been done to the knowledge of the authors.

2. Materials and methods

2.1. Material

The samples used for this study are pure iron cylinders of Φ11 mm diameter obtained by cold crucible melting, which leads to a level of impurities lower than 15 ppm. Fig. 1 shows an optical micrography of the corresponding microstructure. The average grain size is estimated to be 280 μm.

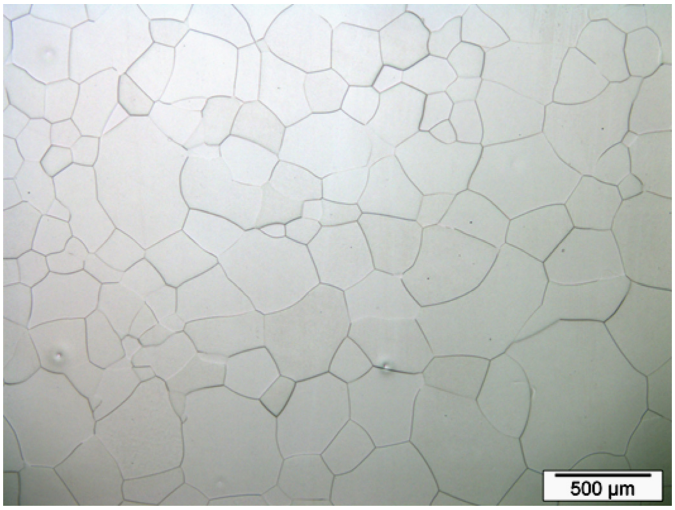

Fig. 1. Optical micrography of the pure iron used.

2.2. Nanocrystallization treatment

The cylinders are cut into 5 mm thick pins as presented in Fig. 2a. Both sides of these pins receive a NanoPeening® treatment. This treatment is a mechanical treatment developed by Winoa group [4] and consists of blasting steel balls (0.1–2 mm diameter) on the sample surface. Nanocrystallization by severe plastic deformation of the near surface is obtained by projecting the balls with an impact angle between 10° and 45° at a speed between 40 and 100 m s^{-1}. The treatment can be of many types, 3 are considered in this study, as shown in Fig. 2b. Table 1 sums up the NanoPeening® treatment parameters.

Table 1
NanoPeening® treatment parameters.

Nomenclature	NN	NPS	NPL
NanoPeening® surface coverage	0%	100%	5000%
Polishing method	Mechanical	None	None
Polishing duration	60 s	0	0
Polishing granulometry	ISO P600	None	None
Abrasive paper material	SiC	None	None

Table 2
Parameters of the nanostructured layer on NPL samples following [23] and [7].

Thickness of the nanostructured layer	60 μm
Minimum grain size	502 nm

The only difference between NPS and NPL treatment types lies in their surface coverage, directly proportional to the treatment duration; the NPL treatment lasts 50 times longer than the NPS treatment. In order to analyze the effects of the mechanical treatment, the reaction of the circumferential surface of the pins has to be negligible compared to the reaction happening on the treated surface. For that purpose, the pins are cut under water into 1 mm thick plates, as shown in Fig. 2c. The surface obtained due to the cutting operation is polished with the same conditions as NN treatment. Then, the prepared samples present a side having received an NN treatment, and another side having received either an NN, an NPS or an NPL treatment.

The nanostructured layer obtained on NPL samples is described in an other study by Lacaille et al. [23] and Tumbajoy et al. [7]. EBSD measurements are coupled to a grain size model as a function of the depth proposed by Tao et al. [3]. Fig. 3b presents the grain size measurements as a function of the depth. The model from Tao et al. is the grain size fit. Hardness measurements carried out by Tumbajoy et al. [7] as a function of the depth show that the hardness improvement due to nanostructuration is located in the first microns. It permits evaluation of the thickness of the nanostructured layer and the minimum grain size as mentioned in Table 2.

2.3. Thermochemical treatment

The nitriding and reduction kinetics is studied using a symmetric thermobalance device (SETARAM TAG-24). The thermochemical cycle is composed of 4 steps as presented in Fig. 4:

1. The increase in the temperature up to 500 °C at 30 °C/min under He.
2. An isothermal reduction step under a mixture of He (3.875 L/h) and H_2 (0.125 L/h) with different durations (from 10 to 360 min).