Modeling nitriding enhancement resulting from the NanoPeening treatment of a Pure Iron.

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Abstract. Nanocrystalline materials are well known to have enhanced diffusion properties, especially due to their high grain boundary density which are fast diffusion channels in the material. In this paper, a highly pure iron sample is treated by NanoPeening® to obtain a nanostructured layer with nanometric grains in the top surface. Then, the grain size distribution is measured by EBSD and optical micrography to fit with an analytical law. It is shown that an exponential law is a good estimator for the grain size distribution after NanoPeening®. Then, using this grain size distribution, the diffusivity distribution is calculated with an analytical model we recently proposed. A 1D finite element simulation of nitrogen diffusion is then performed with this distribution and the concentration profiles are compared with those extracted from a simulation with a constant grain size distribution. Simulations show that NanoPeening® significantly enhances diffusion, dividing the nitriding duration by 2 or by obtaining a 120% gain in the nitriding depth.

1. Introduction

Nanostructured materials are of great interest regarding their effects on mechanical properties [1, 2, 3] and on thermochemical treatments efficiency. As a matter of fact, the material hardness after treatment is improved [4, 5, 6, 7, 8], the nitrogen penetration depth is also increased [5, 6, 9] and for a given penetration depth, the nitriding temperature can be reduced [5, 7, 8]. Friction coefficient [4, 5, 6, 8] and corrosion are also decreased [5].

The NanoPeening® treatment is developed by the Winoa company. It is derived from shot blasting and creates refined grains in the top surface of the material [10]. Figure 1 shows the nanostructured area obtained by NanoPeening® on a 304L stainless steel. One can observe that grains in the top surface are very fine whereas the grains in the bulk material are much larger. In the manner of nanostructured materials obtained with other processes like the surface mechanical attrition treatment or ball milling, the refined grain structure obtained with NanoPeening® improves the efficiency of thermochemical treatments. Figure 2 shows the effect of NanoPeening® after plasma nitriding of 100h at 300°C [10]. One can observe that the penetration depth of nitrogen is improved with NanoPeening®.
The main explanation given for this efficiency improvement in thermochemical treatments is that grain boundaries act as fast diffusion channels in the material [5]. Then when the grain size decreases, the density of grain boundary increases, so it is easier for diffusing elements to travel through the material. The macroscopic diffusivity is then enhanced by the grain boundary higher density. In the literature, there are many homogenization techniques to predict the macroscopic diffusivity knowing the ones in grains and along grain boundaries. A recent work [11] tested few models to simulate the nitriding of an iron treated with SMAT. They tested Hart’s equation [12] which considers a parallel configuration of grain boundaries in the diffusion

![Figure 1. Example of a nanostructured layer on 304L stainless steel [10].](image1)

![Figure 2. Example of the effect of NanoPeening® on 304L Plasma nitriding during 100h at 300 °C. Concentration profiles of nitrogen and carbon for a) coarse grain material b) nanocrystalline material. Optical micrographies of c) coarse grain material d) nanocrystalline material [10].](image2)
direction. They also tried a parallel configuration of grain boundaries perpendicular to the diffusion direction, which is a serial model. They used an Eshelby inclusion-like model [13], a self consistent approach and a geometric average between microscopic diffusivities. They showed that the differences between these models were small and can only be observed with nanocrystalline surfaces, showing the effect of grain boundary configurations. They keep Hart’s equation for their following investigations. We recently proposed a relationship [14] based on Hart’s equation [12] to predict the macroscopic diffusivity taking into account grain boundaries not parallel to the diffusion direction.

The aim of this work is to simulate a nitriding treatment on a nanostructured iron obtained with NanoPeening® by the finite element method using Lacaille’s relationship [14]. Thus, pure iron samples are treated with NanoPeening®, then the nanostructured layer is characterized by optical and EBSD analysis to extract a grain size distribution fitting an exponential law. With this distribution, Lacaille’s model [14] is applied to calculate the diffusivity distribution in the material and then a 1D finite element simulation is conducted to simulate the diffusion of nitrogen in pure iron. A comparison is performed with a constant grain size material to highlight the gain obtained with NanoPeening®.

2. Materials and Methods

2.1. Experimental set up

The samples used are 99.9997% pure iron cylinders of 11mm diameter and 5mm thickness obtained by cold crucible melting. An optical micrography presented in figure 3 leads to estimate the mean grain size at 280µm.

The NanoPeening® treatment performed on the samples used stainless steel spherical particles of 125µm diameter. The optical micrography in figure 4 leads to estimate the thickness of the nanostructured layer at 40µm.

2.2. Grain size distributions

To perform a comparison between a sample treated by NanoPeening® and a coarse grain sample, two grain size distributions are considered. These distributions are functions of the depth x. The first distribution is a constant distribution in order to describe a coarse grain structure.

\[ d(x) = d_2 \]  

(1)
Figure 4. Optical micrography of the nanostructured area.

Table 1. Grain and Grain boundary diffusivities of N in Fe at 300°C [5].

| Parameter | \( m^2/s \)  |
|-----------|--------------|
| \( D_g \) | \( 5.4 \times 10^{-14} \) |
| \( D_{gb} \) | \( 3.3 \times 10^{-11} \) |

where \( d_2 \) is the grain size in the bulk material. The second distribution is an exponential distribution defined for \( x \geq 0 \).

\[
\begin{align*}
  d(x) &= d_1 \left( \frac{dx}{dl} \right)^{l} & \text{if } x \leq l \\
  d(x) &= d_2 & \text{if } x \geq l
\end{align*}
\]

(2)

where \( d_1 \) is the grain size in the top surface and \( l \) the length of the depth affected by nanostructuring regarding the grain size distribution. It is important to notice that this length is different from the nanostructured layer because the grain size under the nanostructured layer is very high considering its thickness, see figure 4. This type of law has been chosen following the measurements carried out by Tao [3]. To extract the corresponding parameters of this law, an iron sample treated with NanoPeening \( \text{"}\text{\textsuperscript{\textregistered}}\text{"} \) has been observed with EBSD technique. The observed area is 50.55µm wide by 35µm deep.

2.3. Diffusion model

To simulate thermochemical treatments, the diffusion equation is used:

\[
\frac{\partial c}{\partial t} = \text{div} \left( D \nabla c \right) \quad (3)
\]

where \( c \) is the concentration of the diffusing element in the material and \( D \) is its diffusivity. This formulation takes into account one diffusing element and does not consider thermodynamical interactions with other elements. Therefore, to differentiate the way atoms diffuse through grains and grain boundaries, there are two different diffusivities in the grains and in the grain boundaries. Table 1 shows these different diffusivities for nitrogen in pure iron at 300°C following the study of Tong [5]. To calculate the diffusivity of the nanostructured layer, Lacaille’s relationship is used [14].

\[
D = D_g + q \frac{\alpha \delta}{d + \alpha \delta} (D_{gb} - D_g) \quad (4)
\]
Figure 5. Concentration contours in a representative cell during transient state simulation of diffusion. The grain and the grain boundaries are differentiated while the diffusion occurs.

Table 2. Grain shape parameters corresponding to equiaxed grains.

| Parameter | Value | Unit |
|-----------|-------|------|
| q         | 0.64  | 1    |
| α         | 3.298 | 1    |

It permits to calculate the effective diffusivity in an equiaxed microstructure knowing the grain size $d$, the grain boundary thickness $\delta$ and both diffusivities at grain $D_g$ and at grain boundary $D_{gb}$. $q$ and $\alpha$ are parameters representative of the grain shape and can also be known. This model is based on the study of diffusion in multiple representative cells as shown in figure 5 and it is very close to the relationship developed by Hart for columnar grains [12], but takes into account grain boundaries not parallel to the diffusion direction. Table 2 shows the shape parameters corresponding to equiaxed grains. These parameters are extracted from a numerical measurement on representative cells generated with NEPER [15]. The grain boundary $\delta$ is estimated to be equal to $\delta = 0.5\text{nm}$ [16].

2.4. Finite elements model
The finite element model is a 1D model with 250 regular elements. The total depth studied is $1\text{mm}$. The computer code Sysweld® [17] has been used to perform simulations. Equation (3) has been used because there is no need to take into account multiple diffusing elements and there are a priori no thermodynamical interactions between Fe and N. On the left, corresponding to the top surface ($x = 0$) a concentration $c = c_0$ has been imposed and on the right ($x = 1\text{mm}$) the concentration has been set to $0: c = 0$. The flow at both ends of the mesh is set to 0. At time $t = 0$ all nodes concentrations have been set to 0. At each element, the diffusivities of its two nodes have been averaged to calculate the diffusivity at the element.
3. Results and discussion

3.1. Grain size distribution

Figure 6a shows the EBSD picture of the observed area. To extract a regular distribution, the depth of the EBSD analysis has been cut into 50 layers of 0.717 µm thick. On each layer, the mean grain size has been obtained by calculating the weighted mean of the grain sizes belonging to the grains whose center of gravity is in the concerned layer. The ponderation coefficients of this weighted mean were the area of each grain. Figure 6b shows the semilog plot of the obtained size measurement and the corresponding size distribution which has been obtained with a linear regression in logarithmic scale to fit with the expression in equation (2). The length \( l \) of the layer affected by nanostructuring, is given by the intersection point of the exponential law and the constant law. Table 3 presents the different laws parameters values, and figure 6b shows a semilog plot of the grain size distributions used to perform the simulations. It appears that with this analysis method, NanoPeening\textsuperscript{R} refines the grains of pure iron to 520 nm. This value is an upper bound of the grain size because due to EBSD precision, some of the smaller grains have not been indexed. This results in an overestimation of the grain size because only the thicker grains have been taken into account in the average calculation. Moreover, this analysis shows that the law chosen for the grain size distribution is in good agreement with the experimental measurements and can constitute a good estimator for further studies.

3.2. Nitriding simulation

Figure 7a shows the normalized concentration profiles \( \frac{c}{c_0} \) in the material after 9h diffusion for both size distributions used. It appears that after NanoPeening\textsuperscript{R} treatment, the nitrogen penetrates deeper indeed into the material than for a constant distribution. Moreover, the
Figure 7. a) Concentration profiles for both size distributions at $t = 9h$. b) Effect of NanoPeening® on diffusion kinetics.

Figure 8. Penetrating depth gain after NanoPeening®.

NanoPeening® profile presents an inflexion point which can be assimilated to a diffusion front. As expected, the distribution which presents the smaller grain size in the surface enables the nitrogen to get deeper into the material. The highest diffusivity in the surface leads to a quick saturation of the nanostructured layer, which appears as a diffusion front on the concentration profiles. To define the penetration depth, it can be assumed that there is a limit concentration $c_p$ above which one can say that the diffusing element has penetrated. Figure 8 shows the gain in the penetrating depth for a sample treated with NanoPeening® compared to a non-treated sample as a function of this arbitrary threshold concentration $c_p$. For $c_p \geq 0.2c_0$, the gain still remains higher than 20%. Moreover, it is noticeable that this simulation is conducted at 300°C. At this temperature range, the diffusivities remain relatively low, which means that the efficiency improvement for the samples treated with NanoPeening® can be much higher than 20%. Figure 7b shows the concentration versus time for both grain size distributions at three different depths: 8µm, 36µm, and 76µm. As expected, one can see that the diffusion kinetics is enhanced by NanoPeening® due to the very fine grains in the top surface. This results in a reduced time to reach a given concentration. For example, for $x = 36µm$, it takes approximately 3.5h to reach a concentration of 0.5$c_0$ with the material treated by NP. For the coarse grain material, it takes approximately 7h to reach the same level of concentration. The gain of 3.5h
is much larger than the NanoPeening® treatment duration which is less than a half hour. For the same reasons explained earlier, this gain would be much higher with a higher temperature.

4. Conclusion
In this paper, an approach to simulate diffusion in nanocrystalline iron taking the grain size into account has been proposed. Microstructural parameters have been determined by optical microographies and EBSD observations. Grain and grain boundary diffusion properties of nitrogen in iron have been extracted from other studies. The homogenization model used has been proposed by Lacaille et al. [14] which is a 3D extension of Hart’s equation. It permits to simulate thermochemical treatments such as nitriding in iron treated with NanoPeening® and to quantify the efficiency improvement. The experimental study of the nitriding process of the same high purity iron is in progress in order to validate this approach or to propose ways for improvement, such as taking into account the grain shape or precipitation for example.

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References
[1] Lu K and Lu J 2004 Materials Science & Engineering, A 375-377 38–45
[2] Roland T, Retraint D, Lu K and Lu J 2006 Scr. Mater. 54 1949–1954
[3] Tao N, Wang Z, Tong W, Sui M, Lu J and Lu K 2002 Acta Mater. 50 4603–4616
[4] Lin Y, Lu J, Wang L, Xu T and Xue Q 2006 Acta Mater. 54 5599–5605
[5] Tong W, Tao N, Wang Z, Lu J and KLu 2003 Science 299 686–688
[6] Tong W, Liu C, Wang W, Tao N, Wang Z, Zuo L and He J 2007 Scr. Mater. 57 533–536
[7] Tong W, Han Z, Wang L, Lu J and Lu K 2008 Surface & Coating Technology 202 4957–4963
[8] Zhang H, Wang L, Hei Z, Liu G, Lu J and Lu K 2003 Z. Metallkd. 10 1143–1147
[9] Gu J, Bei D, Pan J, Lu J and Lu K 2002 Mater. Lett. 340 340–343
[10] Prezeau T, Muller T, Dransart E and Giraud Y 2011 Traitements et Matériaux 412 37–43
[11] Panicaud B, Chemkhi M, Roos A and Retraint D 2012 Applied Surface Science 258 6611 – 6620 ISSN 0169-4332
[12] Hart E 1957 Acta Metallurgica 5 597
[13] Bornert M, Bretheau T and Gilormini P 2001 Homogisation en Mecanique des Materiaux vol 2
[14] Lacaille V, Morel C, Feulvarch E, Kermouche G and Bergheau J M 2014 Finite element analysis of the grain size effect on diffusion in polycrystalline materials. submitted to Computational Materials Science on April 2014.
[15] Quey R, Dawson P and Barbe F 2011 Computer Methods in Applied Mechanics and Engineering 200 1729 – 1745 ISSN 0045-7825
[16] Herzig C and Mishin Y 2005 Diffusion in Condensed Matter (Springer) chap 8, pp 337–366
[17] ESI-Group 2014 User’s manual