Magnetic property approach for identification of dominant crystal structure in AISI420 treated by RF-DC Plasma N₂-H₂

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Abstract. The nitridation of RF-DC plasma N₂-H₂ into AISI420 produces several phases namely α' (bcc), ε (hcp), and γ (fcc) which are randomly distributed in a number that is difficult to identify. So the most dominant justification of crystal phase was needed. Based on the concept of isothermal transformation of AISI420 transformed from the α' phase (ferromagnetic), to ε phase (paramagnetic), and to γ phase (nonmagnetic). It can be used as the underlying theory that magnetic property approach can potentially identify the dominant crystal phase. This study measured the magnetic properties of AISI420 treated by RF-DC plasma N₂-H₂ for identification of dominant crystal structure. Based on the hysteresis curve (M-H loop) of VSM method, magnetic characteristics can be produced such as susceptibility. Furthermore, the atomistic simulations were performed with the LAMMPS. Modelling of schematic picture of the structure using VESTA v.3.3.2 64 bit. Susceptibility value of AISI420 treated with RF-DC Plasma N₂-H₂ is range in the notation of 10⁻⁵ to 10⁻³, so it meets criteria of 10⁻⁵ < 10⁻³ which can be categorized as paramagnetic and super-paramagnetic. It has the dominant ε-Fe₃N phase with trigonal-hcp microstructure based on magnetic property approach and simulations of LAMMPS and VESTA.

1. Introduction

Based on XRD data and microstructure simulations showing the results of nitriding AISI420 with optimization parameters of RF-DC plasma N₂-H₂ in the previous study [1-3] resulted in a heterogeneous random non-homogeneous microstructural phase. Nitridation of RF-DC plasma N₂-H₂ into AISI420 produces several phases namely α' (bcc), ε (hcp), and γ (fcc) [4][5] which are randomly distributed in a number that is difficult to identify. The phase transformation from α' to γ localized at the highly strained slip lines [6]. So the most dominant justification phase which is randomly distributed in a number that is difficult to identify, so the most dominant justification of crystal phase was needed.

Table 1. Summarizes the experimental process parameters for RF-DC plasma N₂-H₂ in the previous study [1-3]

| Process       | Parameters                                                                 |
|---------------|-----------------------------------------------------------------------------|
| Pre-sputtering| DC (-450 V), RF (0 V), pressure (70 Pa), temperature (room standard), duration (400 s), and carrier gas (N₂ only) |
| Nitriding     | DC (-300 V), RF (250 V), pressure (70 Pa), temperature (673 K), duration (5400 s), carrier gas (N₂ + H₂) and with partial pressure (N₂ = 100 ml/min; H₂=20 ml/min) |
This result was confirmed by EBSD analysis using IPF-mapping, KAM, and phase-mapping by Prof. T Aizawa showed that RF-DC Plasma N\textsubscript{2}-H\textsubscript{2} nitriding in AISI420 produced several phases namely $\alpha'$ (bcc), $\varepsilon$ (hcp), and $\gamma$ (fcc) which were scattered randomly in quantities that were difficult to identify [6][7][8][9]. In the high nitrogen content layer, the grain size was greatly reduced by this plastic localization to be less than the spatial resolution by EBSD [6][7]. This results in difficulty of justifying the dominant phase of the material.

In the previous research of V Leskovšek, M Godec, and P Kogej [10] resulting that transformation of the martensitic structure $\alpha'$ $\rightarrow$ $\gamma$ formed by deformation can be identified based on magnetic properties and mechanical strength. Increases in the hardness and percentage of the relative magnetic phase in the $\alpha$ microstructure can be attributed to isothermal transformation during plasma nitriding from the ferromagnetic $\alpha'$ martensitic phase, to paramagnetic $\varepsilon$ martensitic, and to nonmagnetic $\gamma$ martensitic.

The $\alpha$-martensitic structure is a body of cubic (bcc) thus ferromagnetic and as $\varepsilon$ is hexagonal close-packed (hcp) which is paramagnetic. It can be used as underlying theory that magnetic property approach can potentially identify the dominant crystal phase. This study measured the magnetic properties of AISI420 (without nitridation and nitridation with the optimization parameters of RF-DC plasma N\textsubscript{2}-N\textsubscript{2}) for identification of dominant crystal structure using Vibrating Sample Magnetometer.

2. Method

Rectangular samples with 20\times10\times2 mm\textsuperscript{3} of AISI420 specimens were prepared RF-DC plasma N\textsubscript{2}-H\textsubscript{2} behaviour with optimization parameter [2][3][9]. External field value data of $H_{ex}$ in (Oe) and $\sigma$ inner magnetic moment value (emu/gram) of Vibrating Sample Magnetometer (VSM250, Dexion Magnet, Co. Ltd) are presented in the form of hysteresis curve (M-H loop). The curve was analyzed for remanent magnetic moment fluctuations and its coercivity value as an indicator of the occurrence of crystalline anisotropic changes. Based on this method, magnetic characteristics can be produced such as saturation magnetic moment ($M_s$), remanent magnetic moment ($M_r$), intrinsic magnetic coercivity ($H_k$), maximum product energy ($H_{max}$), and susceptibility ($X_v$).

The atomistic simulations presented in this study were performed with the Large-scale Atomic or Molecular Massively Parallel Simulator (LAMMPS), the MD simulator developed by the Sandia National Laboratories [11]. In this study, a three-dimensional system with edge lengths of $L_x$ = 4.56 nm, $L_y$ = 2.85 nm, and $L_z$ = 2.58 nm in the x, y, and z directions, respectively, were simulated. Periodic boundary conditions were applied to all three (x, y, and z) dimensions to model bulk materials such that the total number of atoms was maintained constant during the simulation. The simulation box was filled with iron atoms at the bcc lattice sites (lattice parameter: 0.285 nm). As the energetically preferred sites for nitrogen atoms in an iron monocrystal are octahedral interstitial sites, nitrogen atoms were added randomly to the simulation box at the octahedral sites of the bcc lattice.

The diffusion of nitrogen in iron was modelled using a bcc supercell of 3200 iron atoms with different numbers of nitrogen atoms randomly distributed at interstitials. The interatomic interactions between
Iron and nitrogen were described with a MEAM formulation in which the total energy of the system is specified by [12]:

\[
E = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{ij} \phi_{ij}(r_{ij})
\]  

(1)

where \( F_i \) is the embedding energy function for atom \( i \) embedded in a background electron density \( \rho_i \), and \( \phi_{ij}(r_{ij}) \) is the pair potential interaction between atoms \( i \) and \( j \) separated by a distance \( r_{ij} \). In this research, the potential parameters for the Fe-N system were built according to the 2NN-MEAM interaction potential developed by M I Baskes [12] and B J Lee [13] for pure Fe and N. Modelling of schematic picture of the structure using Visualization for Electronic and STructural Analysis (VESTA) v.3.3.2 64 bit [14].

3. Result and Discussion

The AISI420 without nitridation has a low nitrogen content whereas AISI420 which is crystallized with optimization parameters has a high nitrogen content because it has a higher coercivity value with lower saturation magnetic moments. Low nitrogen content forms alloys in the soft magnetic phase, while in high nitrogen content the average value of saturation magnetic moments decreases and coercivity increases.

![Figure 2](image.png)

Figure 2. Hysteresis curve of AISI420: (a) without nitridation; (b) nitridation.

The saturation magnetic moment value \( (M_s) \) of AISI420 was optimized by the optimization parameter was 1.91 emu/gr.Oe. It can be identified that the microstructure of AISI420 that was nitridation using optimization parameters had the dominant \( \varepsilon \)-Fe\(_3\)N phase. The microstructure of \( \varepsilon \)-Fe\(_3\)N phase is hexagonal close-packed (hcp) type with space P3\(1\)2 \((149)\). The results of this analysis are the same as results of previous studies conducted by S Bhattacharyya [15].

| Table 2. The magnetic property of AISI420 without and with nitridation by RF-DC plasma N\(_2\)-H\(_2\) |
|-----------------|-------------|-------------|
|                 | Without nitridation | Nitridation |
| \( H_{max} \) (Oe) | 22334        | 22364       |
| \( H_k \) (Oe) | 275.43       | 1096.72     |
| \( M_s \) (emu/gr) | 59.82       | 1.91        |
| \( M_r \) (emu/gr) | 12.25       | 0.23        |
| \( M_r/M_s \) | 0.21         | 0.12        |
| Min. \( X_v \) (emu/gr.Oe) | \( 2.67 \times 10^{-3} \) | \( 8.48 \times 10^{-5} \) |
| Max. \( X_v \) (emu/gr.Oe) | 0.21         | 2.52 \times 10^{-3} |

Classification of magnetic material properties consists of ferromagnetic, diamagnetic, paramagnetic, and super-paramagnetic. The nature of magnetic material is identified based on the hysteresis curve
pattern and susceptibility value ($X$). Susceptibility value of AISI420 treated with optimization parameters of RF-DC Plasma $N_2-H_2$ is $8.48 \times 10^{-5}$ emu/gr. Oe up to $2.52 \times 10^{-3}$ emu/gr.Oe. Susceptibility range in the notation of $10^{-5}$ to $10^{-3}$, so it meets criteria of $10^{-5} \leq 10^{-3}$ according to H D Young and R A Freedman [16] which can be categorized as paramagnetic and super-paramagnetic material.

**Figure 3.** Atomic positions of nitrogen (grey) randomly distributed inside iron (blue), modelling of a schematic picture of the structure using Visualization for Electronic and STructural Analysis (VESTA) v.3.3.2 64 bit: (a) space filling’s style; (b) ball-and-stick’s style with show dot surface

**Figure 4.** Deformation of the triangle formed by the hcp directions is indicated from: (a) gives a zoom into the hcp microstructure region $\alpha_1 = 59.48^\circ$; (b) into the fcc region after treated by nitrogen diffusion with $\alpha_2 = 54.09^\circ$

The lattice parameters of iron and iron-nitrogen were calculated using the MEAM potentials in order to verify and validate those potentials. Energy and pressure minimization was carried out using the NVE (constant volume and energy) ensemble with a stopping tolerance for energy and force of $1 \times 10^{-30}$. Relaxation time of 0.1 ps was used for the NVE thermostat. The systems were subsequently heated to different temperatures and equilibrated with the NPT (constant pressure and temperature) ensemble to achieve the desired temperature and pressure.
The NPT simulations were carried out for 25 ps. In order to calculate the displacement of nitrogen atoms at a constant temperature, the NVT (constant volume and temperature) ensemble was used to keep the volume constant throughout the run. The mean square displacement (MSD) of nitrogen atoms in the simulation box concerning their positions in the equilibrated system was recorded for each time step. The total simulation time was set to 1 ns, with a time step of 0.0001 ps. All simulations were performed under zero pressure.

This atomistic simulation results that deformation of the triangle formed by the hcp directions is indicated from $\alpha_1 = 59.48^\circ$ into $\alpha_2 = 54.09^\circ$ after treated by nitrogen diffusion. The deformations were related to extended martensitic lattice by high nitrogen extraordinary solid solution. The phase transformation from martensitic lattice $\alpha'$-Fe through expanded phase into $\varepsilon$-Fe$_3$N lattice-like as in the previous study [1][2].

4. Conclusion
The AISI420 was treated using the optimization of process RF-DC plasma N$_2$-H$_2$ has the dominant $\varepsilon$-Fe$_3$N phase with trigonal hexagonal close-packed (hcp) microstructure in space P312 (149) super-paramagnetic. Classification of magnetic material properties consists of ferromagnetic, diamagnetic, paramagnetic, and super-paramagnetic. The nature of magnetic material is identified based on the hysteresis curve pattern and susceptibility value ($\chi_v$). Susceptibility value of AISI420 treated with optimization parameters of RF-DC Plasma N$_2$-H$_2$ is range in the notation of $10^{-5}$ to $10^{-3}$, so it meets criteria of $10^{-5} < 10^{-3}$ which can be categorized as paramagnetic and super-paramagnetic material. Deformation of the triangle formed by the hcp directions is indicated from $\alpha_1 = 59.48^\circ$ into $\alpha_2 = 54.09^\circ$ after treated by nitrogen diffusion. The phase transformation from martensitic lattice $\alpha'$-Fe through expanded phase into $\varepsilon$-Fe$_3$N lattice.

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