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Short commentary

Review on nitrogen supersaturation into martensitic stainless steels at low temperature

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A plasma nitriding has been utilized as one of the most reliable commercial surface treatment processes, called by "*Ion Nitriding*" and "*Radical Nitriding*," for 40 years (Kuwahara 1992). DC- and DC-pulsed plasmas were used for nitriding of tools, dies and molds and mechanical parts.

A common feature to those plasma nitriding processes is:

1) Higher holding temperature than 773 K.

2) Use of ammonia gas as a nitrogen source.

3) Long processing time to attain the higher surface hardness than 1300 HV and thicker nitrided layer than 80 μm.

4) Formation of chromium and iron nitride precipitates with their high volume fraction when nitriding the stainless steel.

5) Formation of nitrogen diffusion layer with the nitrogen content less than 0.2 mass%. Since the first finding on the nitrogen super-saturation into austenitic stainless steels by the plasma nitriding processes around 673 K (Bell, 2002), many studies on the low temperature plasma nitriding have been reported in the literature (Dong, 2010; Aizawa, 2017; Aizawa,2018), Example: 1) Expansion of η- and a-, or, formation of η-Fe (N) and α'-Fe (N), respectively for AISI304, AISI316 and AISI420 type stainless steels by nitrogen supersaturation; 2) Solid solution hardening without nitride precipitations, and, 3) Only use of nitrogen and hydrogen mixture gas for nitriding.

In addition to reduction of energy consumption during nitriding, this low temperature plasma nitriding provides a new means to improve the hardness and corrosion toughness and to modify the original microstructure. Most of previous studies only stated this improvement of properties; little descriptions were found on the effect of nitrogen super saturation on the inner nitriding behavior, the phase transformation, the induced plastic strains and the microstructure refinement.

The present study utilizes the high density RF/DC plasma nitriding system to drive the nitrogen supersaturation into the martensitic stainless steels respectively at 653 K, 673 K and 693 K for 14.4 ks (Farghali and Aizawa, 2018). This nitrogen super saturation is characterized by α'-phase peak shift in Figure 1, Example: the original peak for α'-Fe (110) significantly shifted to α'-Fe (N) (110). This reveals that α'-lattices expand themselves by the nitrogen solute occupation with the octahedral vacancy sites (Domain et al., 2004).

In parallel to this α'-phase lattice expansion, the austenite peaks are detected in Figure 1, the phase transformation of α'-Fe (N) to η-Fe (N) also takes place with this nitrogen supersaturation. Owing to the high nitrogen ion density as well as high NH-radical population in the plasma sheath, the nitrogen concentration and the hardness at the nitrided substrate surface reach to 30% and 1500 HV, respectively. Figure 2 depicts the nitrogen mapping on the cross-section of the nitrided AISI420 specimen at 673 K.

The inner nitriding process advances homogeneously into the depth of 80 μm. If the inner nitriding process were governed mainly by the nitrogen solute diffusion

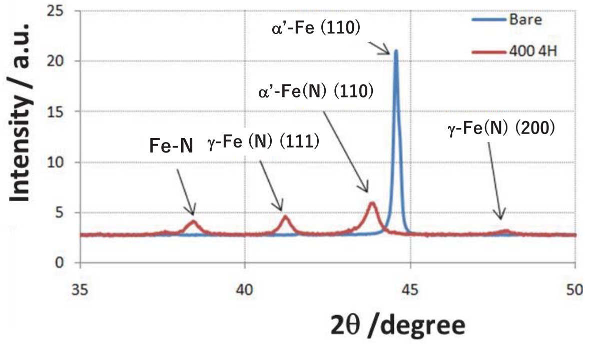

Figure 1: Nitrogen supersaturation is characterized by α'-phase peak shift.

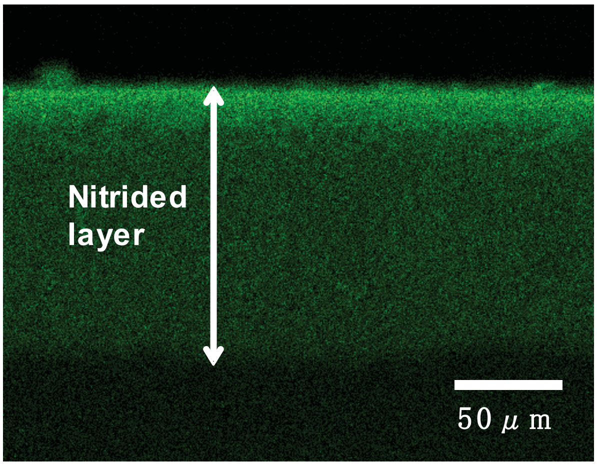

Figure 2: Depicts the nitrogen mapping on the cross-section of the nitrided AISI420 specimen at 673 K.

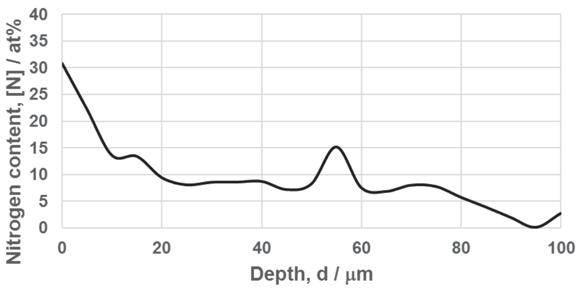

Figure 3: The nitrogen content depth profile has a plateau with constant nitrogen content.

into the depth of substrate, the nitrogen content could exponentially decrease from the surface to the depth as usually observed in the high temperature plasma nitriding processes (Hiraoka and Inoue, 2010). As shown in Figure 3, however, the nitrogen content depth profile has a plateau with constant nitrogen content by 10% in the nitrided layer down to the nitriding front end. This reveals that the inner nitriding process in the low temperature plasma nitriding is completely different from the conventional high temperature plasma nitriding. This difference comes from occupation of diffusing nitrogen solutes with octahedral vacancy sites of α'-lattices in martensitic stainless steels without precipitation reaction into nitrides. This nitrogen content in this plateau is insensitive to the holding temperature; the inner nitriding process is governed by the formation of α'-Fe (N) with high nitrogen content and the nitrogen solute diffusion into the depth of substrate. This new diffusion process is mathematically represented by the diffusion partial-differential equation with the non-linear driving force in the similar manner to the Fisher model (Aizawa, 2017). In particular, when nitriding at 693 K for 14.4 ks, the nitrided layer thickness with more hardness than 1000 HV reaches nearly 100 μm.

The formed α'-Fe (N) has significantly large elastic distortion as measured lattice strain by 5% enough to induce an *in situ* transformation from α'-phase to η-phase. Due to this phase transformation, the nitrided layer from the surface toward the nitriding front end, has α'-η, two phase micro-structure. The average volume fraction of transformed η-phase reaches to 30%. In the transient process of nitrogen super saturation into the depth of matrix, the super-saturated α'-lattices are neighboring to the unsaturated ones. If the lattice distortion took place only in elasticity, there might be a strain incompatibility between the elastically distorted lattices by nitrogen super saturation and the unsaturated ones. Plastic straining is also induced to compensate for this strain incompatibility among two lattices. Phase mapping and KAM (Kernel Average Misorientation) analyses by EBSD (Electron Back-Scattering Diffraction) reveal that transformed η-phase is neighboring to the high strained α'-phase in the nitrided layer. This plastic distortion, induced elsewhere in the nitrided layer, also drives the spin-rotation of constituent subgrains in the nitrided microstructure. The inverse pole figure analysis in EBSD also proves that microstructure refinement also advances from the surface to the depth of nitrided layer by nitrogen super saturation. The average grain size in the nitrided layer reaches to 0.1 μm; the original α'-phase coarse microstructure with the average grain size of 10 to 20 μm changes to fine-grained two-phase microstructure.

Refinement of microstructure in the above significantly increases the grain boundary, which works as a fast rate nitrogen diffusion path as well as α'-Fe (N) lattice. This inter-relation among the lattice expansion of α'-Fe lattices, the phase transformation, the plastic straining, the microstructure refinement and the fast-rate nitrogen diffusion paths drives the low temperature inner nitriding process from the surface to the depth of martensitic stainless steels. As far as this inter-relation works in synergetic as the inner nitriding process, the martensitic stainless steels are efficiently nitrided to have fine-grained two-phase microstructure down to 100 μm in depth with higher hardness than 1000 HV and higher nitrogen content than 5 mass%.

This new characteristics of low temperature plasma nitriding broadens its application in industries and medicals. Hard and fine-grained micro-structure is preferable to surface treatment of martensitic stainless steel molds for injection molding of engineering plastics and mold-stamping of oxide glasses into optical elements. Mold life time is prolonged by high wear resistivity and endurance of these nitrided AISI420 stainless steels against the fatigue cracking. High nitrogen content in the nitrided stainless steels is useful to improve the corrosion toughness as well as the chemical stability. In particular, high nitrogen martensitic stainless steels are precisely machined even by using the polycrystalline diamond (PCD) coated tool to have fine surfaces for mold-stamping. Significant demerits are not found in these applications; more engineering durability must be investigated to make full use of this surface engineering.

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