Diffraction Notes

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QUALITATIVE PHASE ANALYSIS OF NITRIDED STEELS

INTRODUCTION

Many automotive, aerospace, and machine components are subject to wear and abrasion. Common methods of preventing wear and abrasion consist primarily of case hardening methods, particularly carburizing, induction hardening, and flame hardening. Conventional hardening methods have the benefits of increasing wear resistance, obtaining high fatigue life, and, except in the case of stainless steels, resisting corrosion. However, conventional case hardening of steels requires high temperature (>912 C) austenitic/martensitic phase transformation and may cause distortion.

Nitriding is one method of case hardening which results in very low distortion because quenching is not required; moreover, nitriding does not result in phase transformations because it relies upon significantly lower temperatures, typically ranging from 500 to 550 C. During nitriding, a chemical reaction occurs in the diffusion zone producing several hard nitrogen compounds.(1)

A large number of variables influence the nitriding process, including the method of nitriding, temperature, duration of the process, cooling rate, depth of penetration, and type of material being processed. The core hardness of the material may also be affected if the alloy is not specifically intended for nitriding. While a very deep case may not be harmful for wear or failure resistance, developing such a case may not be cost-effective. Optimization of the nitriding process is complex and requires detailed information about the phases formed in the nitrided layer.(2)

ANNOUNCEMENTS

Website Update

All back issues of *Diffraction Notes* are currently available for direct download from our website, www.lambda-research.com. Many of our frequently requested technical papers are also obtainable on-line.

New Appointment

Lambda Research is pleased to announce the addition of Michael Glavicic to our staff. Michael is a recent Ph.D. graduate from McGill University. His thesis work involved texture analysis, stress measurement, and quantitative analysis of films. His main efforts will be concentrated in our Research and Development Laboratory developing new apparatus and techniques.

Patent Awarded

Lambda Research was recently awarded a patent for our automated residual stress profiling apparatus, StressPro℠. The apparatus, developed primarily for quality control and process development, permits two subsurface residual stress distributions to be generated in as little as an hour.

For more information about our testing capabilities, accreditations, or other publications, visit our website at www.lambda-research.com.

Lambda Research is an accredited independent laboratory providing unique x-ray diffraction and fluorescence testing and research services to industrial, government and academic clients since 1977.

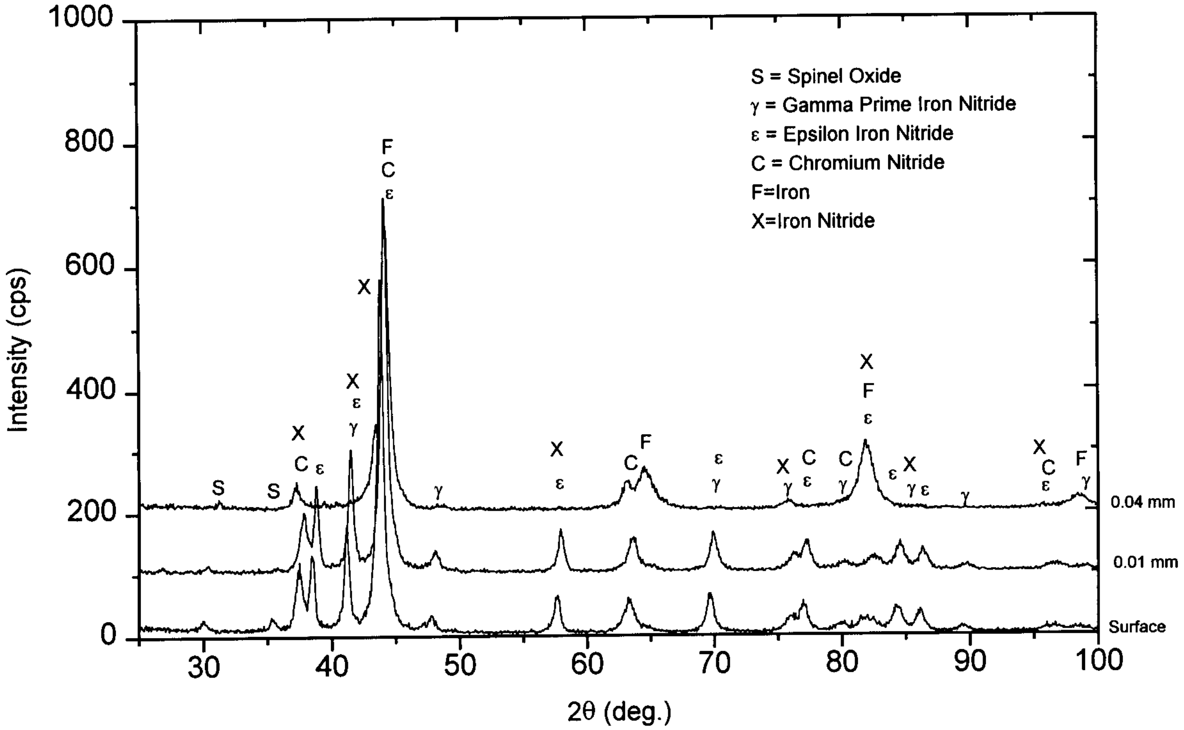

Fig. 1: Series of overlaid diffraction patterns of a nitrided sample.

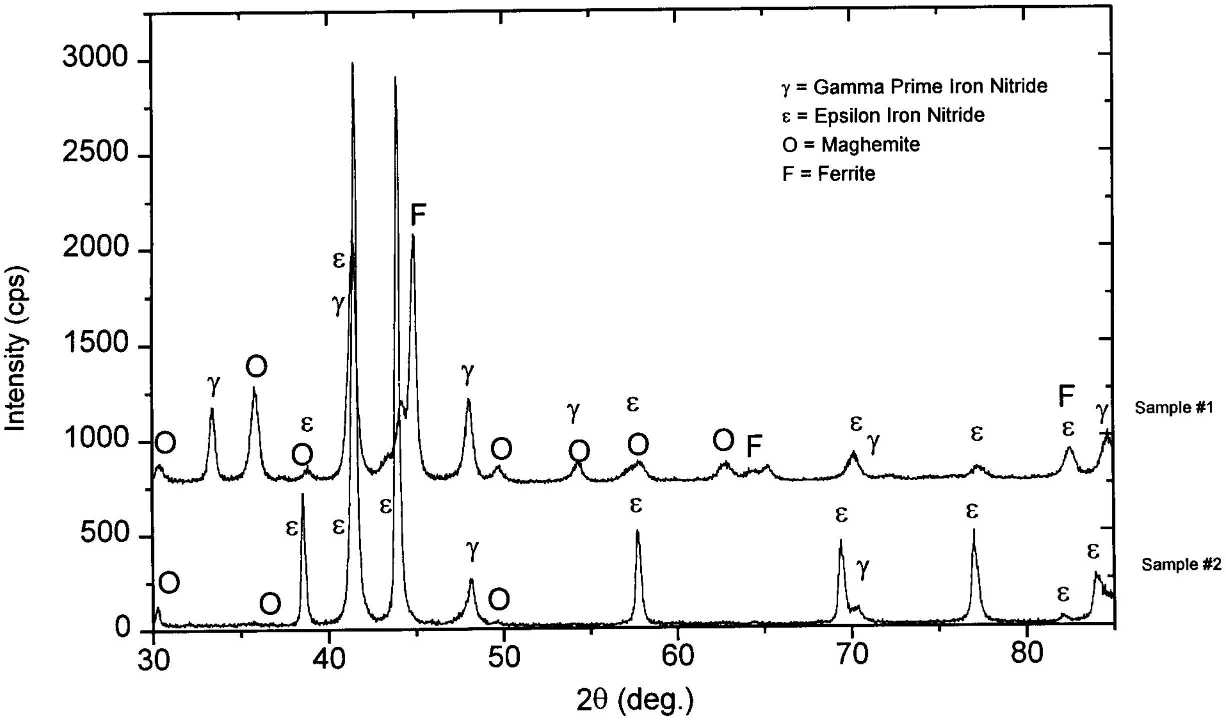

Fig. 2: Surface diffraction patterns in two nitrided specimens.

Four primary means of nitriding exist: gas, liquid, powder, or plasma assisted. Of these, the most common are gas nitriding, liquid nitriding, and ionitriding, a form of plasma nitriding. In gas nitriding, ammonia diffuses into the steel and produces an undesirable porous white layer on the surface of the component. Double gas nitriding can be used to produce a thinner, softer, and more ductile white layer. Liquid nitriding requires the application of molten cyanide-cyanate salts and tends to produce the beneficial, ductile epsilon phase of iron nitride without the white layer.(1) Ionitriding utilizes ionized nitrogen gas to implant the ions into the surface. Although the white layer is produced, its formation can be controlled.

NITRIDED CASE AND LAYERS PRODUCED

The depth and hardness of the nitrided case depend upon the amount of nitride-forming elements in the material, such as aluminum, chromium, molybdenum, and vanadium. When large amounts of these elements are present, the case tends to be thinner and very hard. Conversely, when the concentration is reduced, the case tends to be deeper and softer.(3) The presence of aluminum in steel causes the development of a very high hardness and provides excellent wear resistance and low case ductility. Low alloy chromium steels create a more ductile case and lower hardness than is achieved in aluminum-containing steels. Molybdenum reduces the likelihood of temper embrittlement. Nitriding is also applicable to tantalum and titanium alloys.

The nitrided case consists of three layers, namely, the "white layer," the compound layer, and the diffusion layer. The white layer, produced in gas nitriding, is Fe_2N (orthohombic structure). The white layer is a very thin (0.005 mm to 0.05 mm), porous, brittle tier located on top of the compound layer. While valuable for improving corrosion resistance, the white layer is generally removed by mechanical polishing in order to increase wear resistance. The compound, or functional, surface layer is located below the white layer and may contain nitrides and carbon nitrides of types Fe_4N (gamma-prime iron nitride, cubic structure) and $Fe_{2-3}(N,C)$ (epsilon iron nitride, hexagonal) and nitrides formed from nitride-forming elements in the material. The wear resistance of the compound layer is influenced by its composition and crystal structure. Generally, a higher percentage of the epsilon iron nitride, $Fe_{2-3}N$, is desirable. The nonporous diffusion layer, which is below the compound layer, is a combination of nitride dispersions and nitrogen in interstitial solution in the ferrite or martensite matrix. The nitriding depth in the diffusion layer influences the wear resistance.(2)

Because the nitride layer's crystal structure and composition depend upon the nitriding parameters and govern the properties of the surface produced, x-ray diffraction is a useful tool for obtaining information

COMMON PHASES IDENTIFIED BY
X-RAY DIFFRACTION IN NITRIDED SAMPLES

Phase	Formula	PDF#	Structure
Chromium Nitride	CrN	11-65	Cubic
Epsilon Iron Nitride	Fe_3N	3-925	Hexagonal
Gamma-Prime Iron Nitride	Fe_4N	6-627	Cubic
Ferrite (Iron)	Fe	6-696	Cubic
Spinel-Type Oxide (e.g., Magnetite)	Fe_3O_4	19-629	Cubic
Maghemite-Q	Fe_2O_3	25-1402	Tetragonal

Table I

about process development and control of nitriding.(2) X-ray diffraction can be used to identify which phases are present at the surface and the distribution of those phases with depth below the surface of the nitrided component. Lambda Research has developed techniques for making measurements as a function of depth in increments as small as 2.5 μm (0.0001 in.).

ANALYSIS

Diffraction patterns obtained on nitrided samples typically contain one or more of the following: gamma-prime iron nitride, epsilon iron nitride, chromium nitride, iron (ferrite or martensite), and spinel-type oxide (e.g., magnetite). The desirable epsilon phase of iron nitride is tough and ductile, but not brittle. Table I lists additional information concerning these phases. Additional nitride phases have also been observed.

Figure 1 shows a series of overlaid diffraction patterns of a nitrided sample. The "surface" pattern was taken on the as-received surface of the part. Diffraction patterns were also obtained at depths of 0.01 mm and 0.04 mm. The measurement depths can be achieved by electropolishing or metallurgically polishing, as applicable. Both polishing methods are routinely performed at Lambda Research.

Diffraction patterns were obtained using graphite monochromated copper K-alpha radiation on a computer controlled, Bragg-Brentano focusing geometry horizontal diffractometer. The x-ray diffraction patterns were analyzed using first and second derivative algorithms, after Golay(4) digital filter smoothing, to determine the angular positions and the absolute and relative intensities of each detectable diffraction peak.

NBS standard reference material No. 675, "Low Two-Theta Standard for X-ray Powder Diffraction," was employed to correct systematic error in the diffraction angle caused by instrument misalignment and aberrations due to defocusing, beam divergence, etc.

As seen in Figure 1, as the depth increases, the spinel-type oxide, epsilon iron nitride, and gamma-prime iron nitride contents diminish until they are virtually undetectable or reduced to only trace phases. The peaks for chromium nitride, although decreasing in intensity, remain visible on the diffraction pattern at the 0.04 mm depth. Note that, as more material is removed, the intensity of the underlying iron (steel) peaks increases.

The data shown in Figure 2 illustrate the differences that can occur when nitriding parameters are varied. The beneficial epsilon iron nitride phase dominates the pattern for Sample 2, which indicates that the epsilon phase was the major constituent on the surface. The diffraction patterns also indicate that the nitride layer is thicker for Sample 2, as compared to Sample 1, because of the underlying ferrite peaks detected on the pattern for Sample 1. The shift in the epsilon iron nitride peaks, especially for Sample 2, are associated with the changes in the stoichiometry.

SUMMARY

X-ray diffraction is a viable method for determining the phase composition of a nitrided case both at and beneath the surface. The comparative thickness of the coating can also be attained using depth analysis. Lambda Research provides sample preparation and sample analysis capabilities suitable for both nitriding process development and quality control.

REFERENCES:

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(2) ASM Handbook: Friction, Lubrication, and Wear Technology, S. D. Henry, ed., vol. 18, American Society for Metals, Materials Park, OH, 1992.

(3) Metals Handbook, Properties and Selection: Irons and Steels, B. B. Bardes, ed., vol. 1., 9th edition, American Society for Metals, Metals Park, OH, 1978.

(4) Golay, M., *Anal. Chem.*, Vol. 36, 1964, p. 1627.