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An investigation of spalling of case-hardened Nitralloy

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Spalling of nitralloy (balance Fe, 0.42% C, 0.55% Mn, 0.3% Si, 1.6% Cr, and 1.0% Al) during grinding has been studied. It was found that excess nitrogen which diffused into the α-Fe lattice during a two-step nitriding process was responsible for making the alloy surface brittle. This caused the spalling of the alloy during a subsequent machining operation. Practically feasible ways to avoid this problem have been discussed.

1. Introduction

The nitriding process has been widely used for many decades. During that time, a trade-off had to be accepted. Part cases could be made hard, corrosion resistant, and abrasion resistant, but often they were too brittle to machine or even handle. In this research, solutions were found to minimize that trade-off. A nitrided part can have a hard coat and also be manufacturable.

The authors noted that little information exists in the body of published work that directly concerns nitriding damage. Even fewer studies discuss any serious means with which to limit that damage. The ASM Handbook [1] mentions one way to reduce spalling (i.e. chipping or cracking at the edge) of nitrided parts: the parts must be designed to have no sharp edges, which is not a possibility in the present case. Jain *et al.* [2] discussed the influence of grinding wheel hardness or chipping of steels. They found that use of H grade or softer grinding wheel did not cause any cracking when grinding hardened low-alloy steel. According to *The Source Book on Nitriding* [3], chipping can be reduced by post-nitride annealing; however, no explanation of justification is provided.

The parts in question are small spool valves: about 75 mm long and <25 mm diameter. These valve spools are made from Nitralloy 135 M steel by the Hamilton Standard Division of UTC for use in aviation fluid-control systems that require very accurate fluid-control characteristics. The edges of the lands of the spool, which allow or deny fluid passage, have to be extremely clean and accurate. In addition, because the spool slides within a sleeve to form a functioning valve, the spool lands must meet a minimum requirement of wear resistance or surface hardness. The production of these spool valves requires that the Nitralloy bar stock go through several manufacturing operations (described later). The last operation is a dry grinding of the sides of the lands to match their thickness to that required by the ports in the sleeve, and to leave the lands with corners of radii <25 μm to make fluid-control properties uniform and predictable. At this point, after some $3000 has been spent on the production of this spool sleeve combination, the spalling occurred, and the valve was rejected.

We have investigated the cause and mechanism involved in the spalling of nitrided surfaces to suggest economically viable solutions to eliminate this chipping. This analysis included (1) scrutiny of each operation in the manufacturing cycle, (2) subsurface metallurgical analysis of parts after each step in the manufacturing cycle, and (3) surface analysis of the final product.

2. Experimental procedure

A test part was designed to model an average nitrided valve spool (Fig. 1). The part had eight, sharp, nitrided edges, which are the specific areas in the production parts where the spalling occurred and caused the valves to fail inspection.

A representative manufacturing cycle, including a two-step nitriding process, was designed to fabricate 15 test parts from 35.6 mm Nitralloy 135M (AMS 6470) bar stock. The manufacturing cycle included all the steps that Hamilton Standard normally uses in a typical production cycle of a spool valve. All of the manufacturing steps were performed at Hamilton Standard's Windsor Locks facility, while the analysis was conducted in the Surface Integrity Laboratory at the University of Connecticut's Center for Grinding Research and Development. At the end of each major manufacturing operation, one part was removed from the manufacturing cycle for analysis.

The major steps in the original manufacturing test cycle are described below.

1. Fifteen test part blanks were created from Nitralloy 135M bar stock, drawn from Hamilton Standard inventory.

2. The parts were turned to within 0.75 mm of the final diameter of the surfaces to be nitrided.

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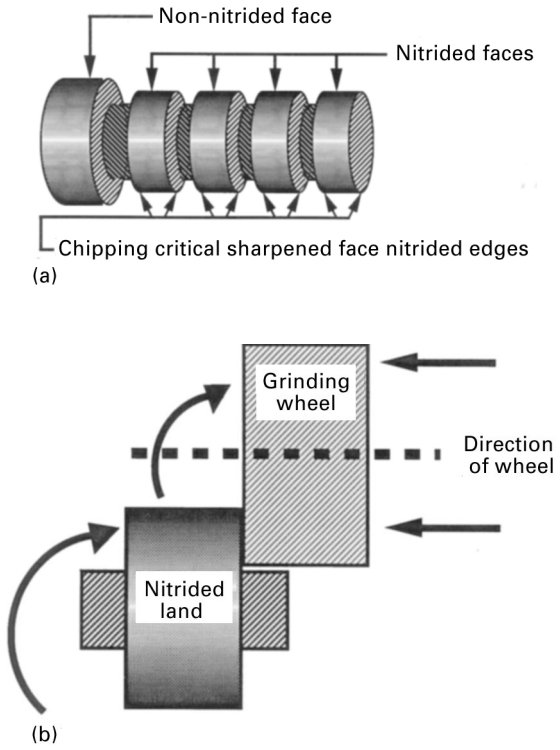

Figure 1 (a) Manufacturing the test part. (b) An isolated land, and spalling critical land grinding.

3. The parts were heat treated 965 ± 14 °C for 1.5 h, oil-quenched to obtain a uniform, martensitic structure, and tempered at 620 ± 14 °C for 2 h to obtain a uniform, tempered martensitic structure with a hardness of 30–36 Rockwell C.

4. The parts were semi-finish-turned to create and place the lands within 125 μm of their final diameter.

5. The parts were stress-relieved at 620 ± 14 °C for 2 h to remove residual stresses imparted during the turning operations.

6. The whole surface of each part was plated with copper to a thickness of 38 μm to block nitrogen diffusion in undesired areas during the nitriding process.

7. The copper plate was then removed from the surfaces to be nitrided to produce an acceptable nitriding surface. This was accomplished by grinding the land surfaces with a maximum diameter reduction of 55 μm, leaving them within 70 μm of their final diameter. All parts were analysed for residual stresses.

8. The test cycle was split to determine if the pre-nitride residual stresses play a significant role in the post-nitride spalling. Two parts were removed from the test cycle, stress relieved at 637 ± 5.5 °C for 2 h, analysed for their stresses, and returned to the cycle.

9. The test parts were nitrided in a two-step process.

(i) Step 1: 537 ± 5.5 °C for 7 h with an ammonia dissociation rate of raw (uncontrolled).

(ii) Step 2: 565 ± 5.5 °C for 15 h with an ammonia dissociation rate of 70%–75%. All parts were analysed for residual stresses.

10. Two of the nitrided parts were vacuum annealed at 650 ± 2.75 °C for 2 h and returned to the cycle.

11. The copper plate was chemically stripped. The surface grind was performed on the lands, with a maximum diameter reduction of 120 μm, placing the lands in their final diameter.

12. The final step was a grinding operation that sharpened the critical edges of the lands (Fig. 1b). This process was performed by bringing a rotating grinding wheel into contact with the side of the lands. This final grind was done without grinding fluid and by optically controlling the operation at $\times 10$ magnification to ensure proper size and corner radii of the lands. All remaining parts were removed for analysis and chip detection.

Between many of the major steps listed above, various minor procedures were performed that were not critical to the research and thus are not reported. These processes included vapour degreasing, demagnetizing, hardness checking, deburring, preserving, packaging, and centring.

The test parts removed from the manufacturing cycle after various steps were subjected to metallurgical analysis. X-ray diffraction was used for residual stress and phase analysis. The microstructure and spalling were observed under an optical microscope. The bulk and microhardness testers were used to obtain the Rockwell C hardness and microhardness profile within the nitrided layer.

Inspection of the test parts after final grinding revealed that the two specimens that were vacuum-annealed after nitriding did not spall at all; all other specimens badly chipped during the final grinding. Surface analysis of the parts immediately after nitriding and annealing indicated higher concentrations of nitrides in nitrided parts than in annealed parts (Figs 2 and 3)

These results of the original manufacturing test cycle indicated a possible problem and two probable solutions. The possible problem was believed to be excessive nitriding. One solution, as is apparent from the previous discussion, is to vacuum-anneal the excessively nitrided parts. The other probable solution entailed closer adherence to the nitriding guidance recommended in the literature [1], a procedure that is considerably less aggressive than the nitriding process used in the original manufacturing cycle.

Thus, a modified manufacturing cycle was designed that followed the process of the original cycle with the following exceptions.

1. A sample part was not removed after each major step in the process.

2. A less aggressive nitriding process (as recommended in ASM Handbook) was used, which is approximately as follows:

(i) Step 1: 510 °C for 7 h with an ammonia dissociation rate of 25%–30%.

(ii) Step 2: 565 °C for 12.5 h with an ammonia dissociation rate of 70%–75%.

Out of the three groups of parts (e.g. aggressively nitrided parts from original manufacturing cycle, aggressively nitrided and annealed parts, and less aggressively nitrided parts from modified manufacturing cycle) during these two manufacturing runs, two groups (each with 16 sharpened edges) displayed

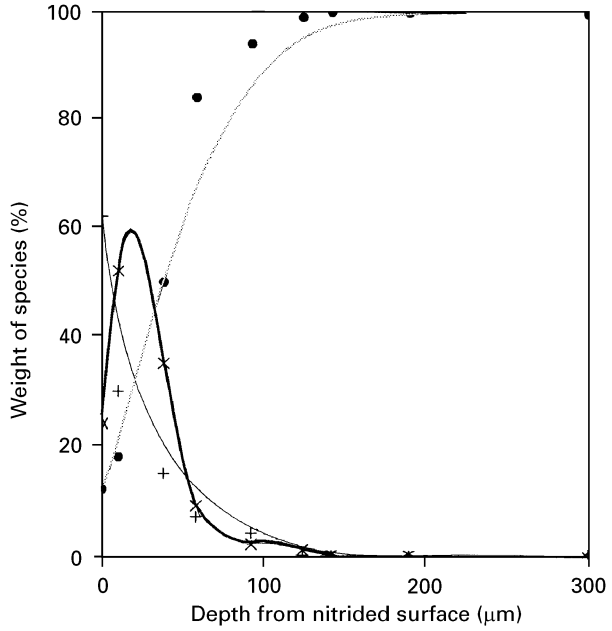

Figure 2 Phase versus depth profiles: aggressive nitrided parts. (×) Austenite (——), (+) Fe_4N (——), (●) ferrite, (·····).

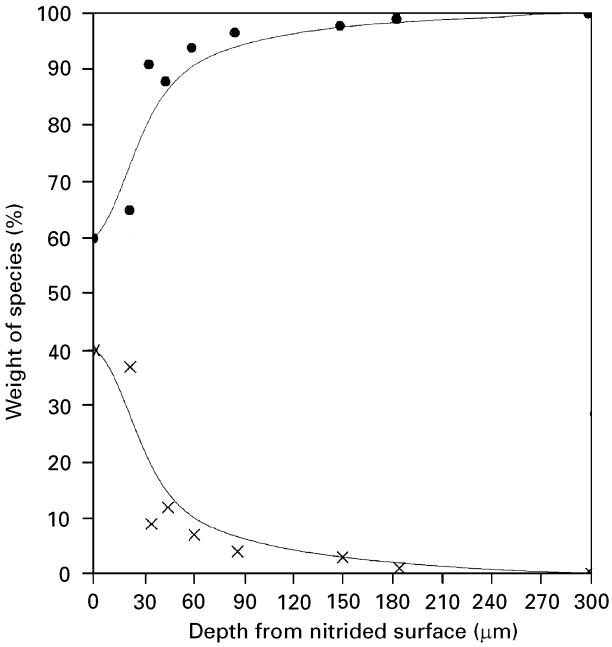

Figure 3 Phase versus depth profiles: aggressive nitrided and annealed parts. (●) Ferrite, (×) austenite.

a marked reduction in chipping: the aggressively nitrided and annealed parts and the less aggressively nitrided parts. To determine what was causing the chipping reduction, the metallurgical analyses were performed as described before. In addition, surveys into the surfaces of the parts were performed by using X-ray diffraction to determine the phases present and lattice parameters of the phases involved. Between each X-ray analysis, electro-polishing was used to remove small, 5–40 μm, layers without damaging the freshly exposed surfaces. The X-ray and electro-polishing cycle was repeated until the effects of the diffused nitrogen could no longer be detected. The results of these surveys are shown in Figs 2–5.

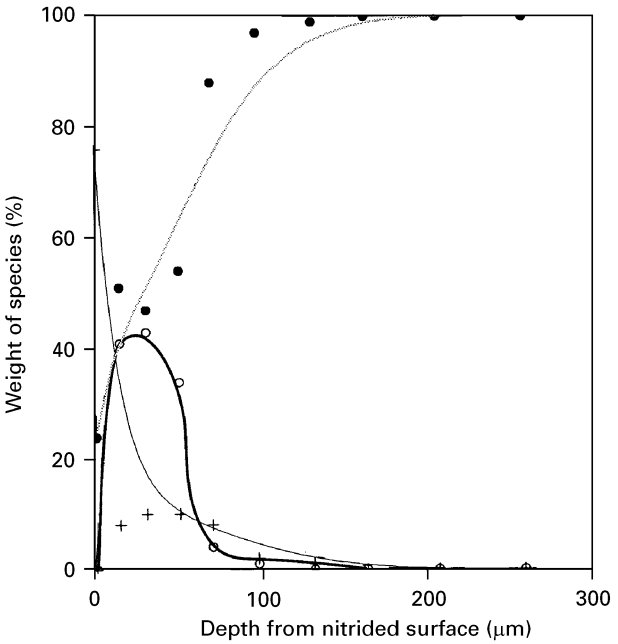

Figure 4 Phase versus depth profiles: less aggressive nitrided parts. (●) Ferrite, (·····), (+) Fe_4N iron nitride (——), (○) $Fe_{2-3}N$ iron nitride (——).

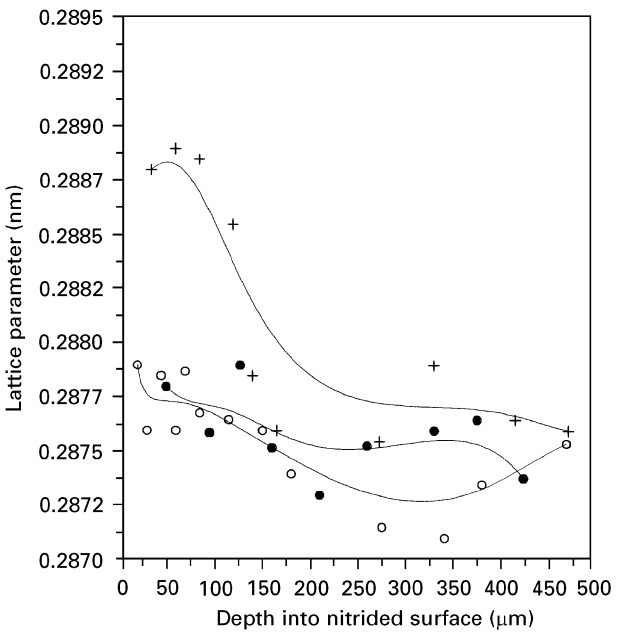

Figure 5 α-Fe lattice parameter profiles. (+) Pre-anneal *a*-spacing, serious chipping; (○) post-anneal *a*-spacing, no chipping; (●) good nitride *a*-spacing, no chipping.

3. Discussion

As mentioned above, two groups of parts displayed greatly reduced chipping. The post-nitride annealed parts showed an 11-fold reduction in total spalling, and the modified test-run parts showed a 35-fold reduction in total chipping. Additionally, both groups displayed no chips large enough to cause rejection.

Few differences existed between the parts that chipped and the parts that did not chip. In fact, all three groups of parts had:

(i) similar bulk hardness and micro-hardness versus depth characteristics (Fig. 6);

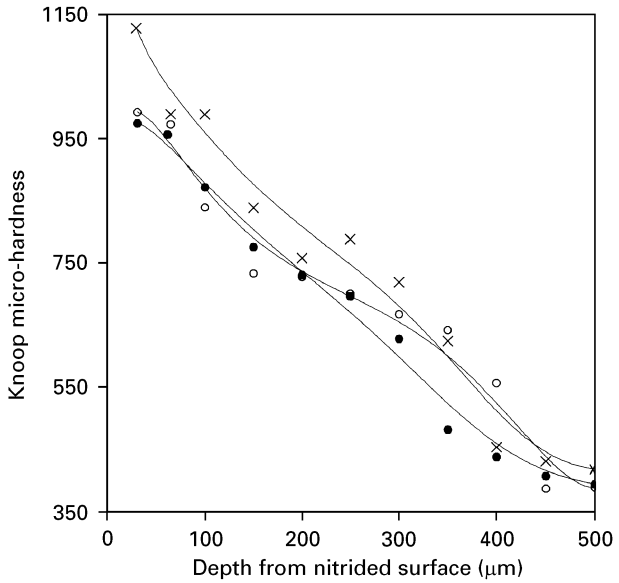

Figure 6 Hardness versus depth profiles. (●) Less-aggressive nitride, (×) aggressive nitride, (○) aggressive nitride and anneal. Bulk hardness: aggressive nitride, 31.9 Rc; aggressive nitride with anneal, 29.9 Rc.

(ii) similar near-surface compressive residual stresses;

(iii) similar case depths;

(iv) identical microstructures;

(v) no apparent correlation between phases present (α-Fe, γ-Fe, γ′-iron nitride and ε-iron nitride) and chipping (Figs 2–4).

The only conclusive differences were in their chipping characteristics and their α-Fe lattice parameters, which represents a measure of nitrogen dissolved in solid solution within the α-Fe (Fig. 5).

The results of the phase versus depth surveys and the α-Fe lattice parameter surveys showed that the presence of various nitride and iron phases or their relative concentrations had little effect on the embrittlement of the nitride case. But the nitrogen atoms diffused into the bcc iron lattice in the form of an interstitial solid solution, appear to cause sufficient embrittlement to cause the spalling. Because α-Fe can dissolve only a very small amount of nitrogen in solid solution under equilibrium conditions at ambient temperatures, the lattice parameter should not exceed 0.288 nm. This is the value of the lattice parameter of α-Fe at the bottom of the nitrided case for all three groups of specimens, as can be seen from Fig. 5. It is assumed that, at this depth, a near-equilibrium amount of nitrogen is dissolved in the α-Fe lattice. Also note that the α-Fe lattice parameter for carbon steels is about 0.2867 nm and about 0.2869 nm for Nitralloy 135M, as established by an X-ray diffraction experiment performed on nitralloy before nitriding.

All of the chipped samples displayed a near-surface lattice parameter of nearly 0.289 nm, which indicates a super-saturated α-Fe solid solution. Alternatively, this parameter indicates that significantly more nitrogen is present in the α-Fe host lattice than α-Fe can usually dissolve under equilibrium conditions. This unusually large amount of dissolved nitrogen had considerably distorted the α-Fe lattice, the effect of which would be to impede the dislocation movement and, in turn, to cause the embrittlement that leads to the chipping.

The annealed and less aggressively nitrided parts have near-surface lattice parameters in the range of 0.2875–0.2880 nm, nearly a full 1000th of a nanometer below that of the chipped parts. This indicates that significantly less nitrogen exists in solid solution near the surface of the unchipped parts than in the chipped parts. This reduced nitrogen dissolution results in reduced lattice distortion, and hence reduced embrittlement, which consequently leads to a greatly reduced likelihood of spalling.

Finally, it can be concluded from Fig. 6 that nitriding with a less aggressive nitriding cycle or annealing of aggressively nitrided parts does not result in significant hardness loss. These parts still remain within the hardness specification for the intended use.

4. Conclusions

1. Spalling of sharpened nitrided corners is not inherent to the nitriding process. The current investigation found that sharp corners with radii <25 μm can be produced without spalling.

2. The use of a less aggressive nitriding process eliminates the spalling problem.

3. The use of a post-nitride anneal can render even seriously embrittled parts usable again.

4. The chipping seems to be caused by an excessive amount of nitrogen dissolved in the α-Fe lattice, causing the α-Fe solid solution to embrittle and making the steel susceptible to spalling.

5. The concentrations of various nitride phases or austenite in the nitrided layer do not seem to have any noticeable effect on embrittlement of steel and hence on chipping or spalling.

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