Method for Analyzing Nitrogen in Titanium Alloys

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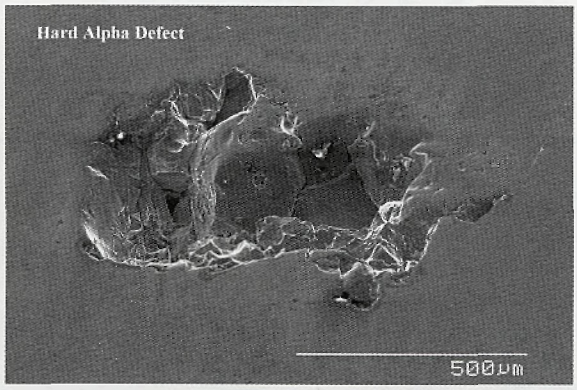
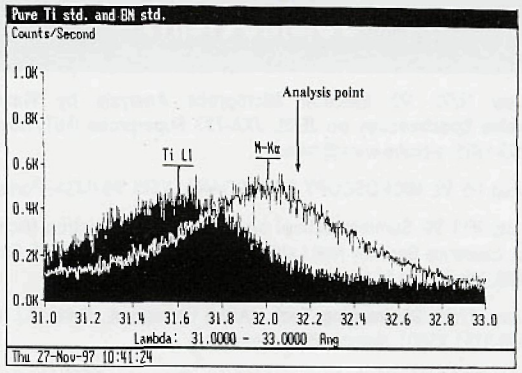
Careful analysis of the composition of the titanium alloys is a very critical part of the overall quality control of all components in modern jet aircraft engines. The engine manufacturing industry is seriously striving for a zero defect rate, which is a very difficult goal indeed. This control is made more difficult by the very reactive nature of titanium when it is heated to its melting point. Titanium reacts with the nitrogen and oxygen in the air to form brittle refractory compounds, so it must be melted and refined in a vacuum. Once these refractories are formed they are very difficult to find or remove and they form the basis for brittle zones in the alloy that can be the initiation site for cracks under the high stress loads found in a jet engine. The presence of nitrogen, in particular, causes a defect called a "hard-alpha", which is an area of nitrogen enrichment containing three to eight percent nitrogen and having a hardness three times that of the alloy[1]. It is characterized by the exclusion of the alloy additions which give the titanium its high temperature strength. Around the defect, where the nitrogen content diffuses down to zero, there forms a zone of brittle, alpha-phase material which propagates the cracks which form in the defect.[2]



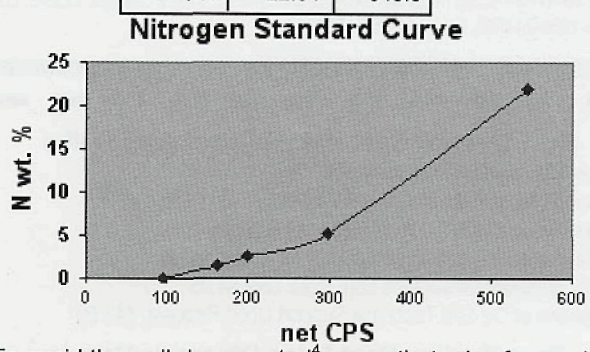
In this SEM micrograph of a hard-alpha defect, we can see that the center is the defect site, where brittle material has fractured away. The zone around the defect, which is highly reflective in the optical microscope, is the brittle alpha phase, where the strengthening alloy additions are reduced. The center is where the crack would initiate and then cracks would grow in the surrounding alpha phase.

Research into these hard-alpha defects requires an accurate diffusion profile of all the elements in the defect, in the alpha zone surrounding it and out into matrix to measure the extent of the affected volume. The preferred method is usually wavelength-dispersive x-ray (WDX) analysis, since it is precise, works on a small volume and can test for all the elements in question[3]. The usual practice is to do a line of analyses from the defect into the matrix metal to get a diffusion profile. The problems of nitrogen analysis are that this is a very light element so the characteristic x-rays are very soft and are preferentially absorbed by carbon-containing surface films, contamination and the thin window of the x-ray detector[4]. The operating conditions of the microprobe for the nitrogen analysis are 10kV accelerating voltage and 400 nA beam current, which causes contamination and is a difficult condition to stabilize on most microprobes.



The biggest problem in analyzing nitrogen in the presence of titanium is the serious overlap of the nitrogen Kα peak with a minor peak of titanium, the L_l peak.[4] This WDX spectrum of pure titanium and boron nitride shows the extent of the problem. In the alloys used for jet engines, the titanium content is usually around 90 weight percent, so even this minor titanium peak seriously interferes with nitrogen determination. We found that carefully analyzing off the peak centroid to minimize the overlap gave the best chance of maximizing the nitrogen response. The nitrogen peak is broad and moving to the location as high as possible on the peak while avoiding the overlapping line provides a reasonable nitrogen response while minimizing the overlap. The background counts are taken on pure titanium at the same location as the off-peak nitrogen Kα reading[3], providing usable detection limits of 0.25 weight percent nitrogen in the Ti6,4 titanium alloy studied (6% Al, 4%V and remainder Ti) and reproducibility of +/- 0.01 % at these levels.

Nitrogen Standard Curve		
	Net wt %	Net CPS
Pure Ti	0	94.1
	1.47	162.1
	2.61	199.8
	5.18	298.4
TiN	22.04	545.5



To avoid the well-documented[4] errors that arise from calculating the atomic (Z) number, absorption correction and fluorescence (ZAF) correction factors for a very light element in a heavier matrix, a standard curve of nitrogen content was constructed. Since the hard-alpha zone is just Ti and N, which form an alpha-stabilized phase over a large range of concentrations, it turned out to be relatively easy to make homogeneous standards by sintering together exact amounts of C.P. Ti and carefully analyzed, stoichiometric TiN (22.04% N). The fine powders of Ti and TiN were thoroughly mixed and sintered together in a vacuum furnace at 900° C. for periods of up to a week to get a completely diffused

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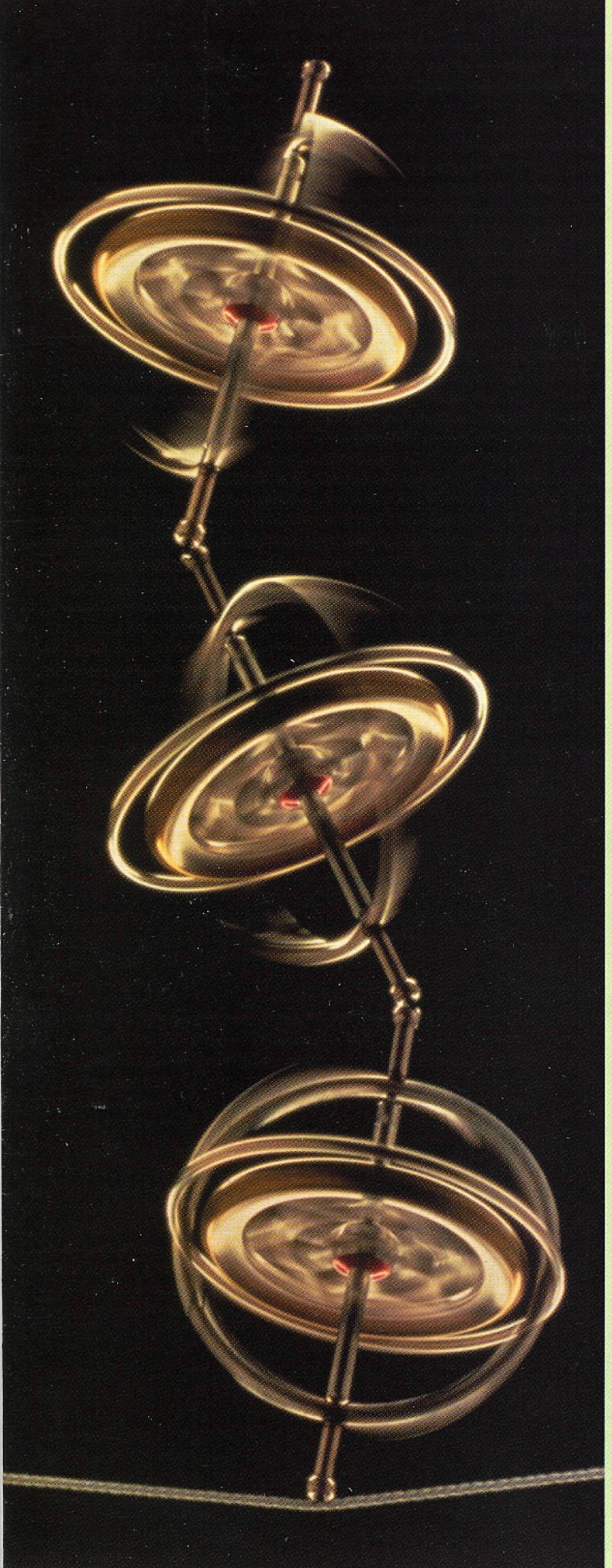

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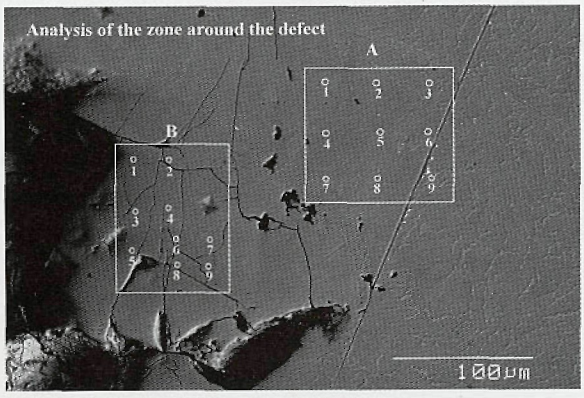
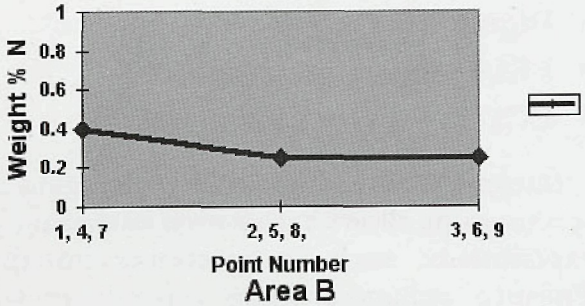
block of known nitrogen concentration. The nitrogen content of the unknowns was read off of this curve.

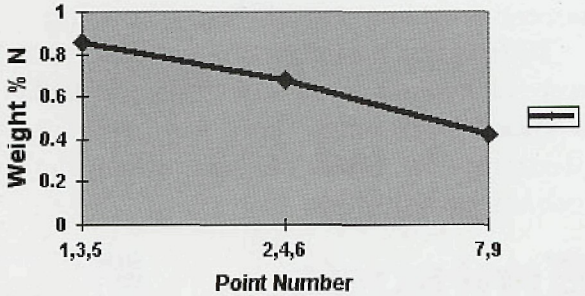
In the next, back-scattered electron (BSE) photo, the corner of the previous hard-alpha photo can be seen, with the cracking of the alpha phase evident. The normal, alpha-beta structure of the Ti6,4 matrix can be seen outside of the alpha zone. Hardness indentations were made to associate the hardness with the nitrogen content. Two sets of multi-point analyses were made to trace the decrease of nitrogen as we move away from the defect towards the junction of the alpha phase and the alpha-beta matrix. These analyses were also used to relate nitrogen content to micro-hardness readings. The results show the decrease in nitrogen content as we move away from the brittle defect area and clearly show the relationship of nitrogen content with crack propagation in the alpha zone around the defect. Even the highest content seen, close to the hollow formed by the defect, is below 1% nitrogen and in Area A the measurements quickly drop to the detection limit of 0.25 % N.



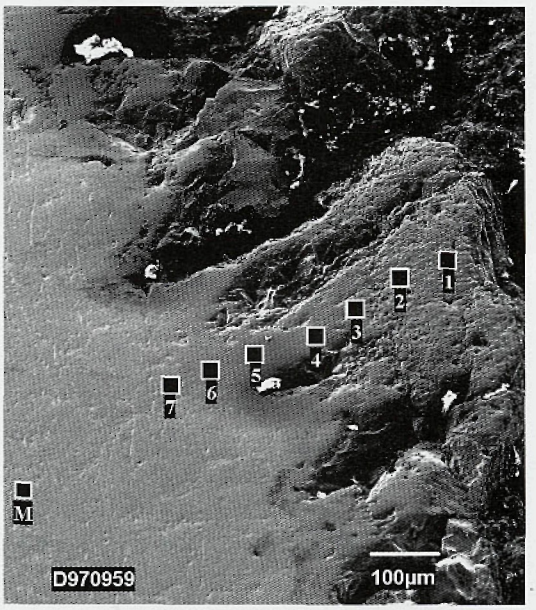
Area A



Area B



Since developing this technique we have analyzed many defect samples, both from our own research and from titanium alloy producers, in both double VAR (Vacuum Arc Re-melting) and triple VAR samples. The low detection limit and reproducible profiles of nitrogen and the other alloy components are proving invaluable to fully characterize the diffusion profile of hard-alpha defects.



Point Number	N wt.%	Al wt.%	V wt.%
point 1	12.43	N.D.	N.D.
point 2	11.01	N.D.	N.D.
point 3	10.29	N.D.	0.35
point 4	5.95	2.18	0.88
point 5	1.35	7.27	2.73
point 6	1.91	8.43	1.24
point 7	2.15	7.06	3.41
point M	N.D.	6.24	2.24

This sample of a double-VAR Ti6,4 alloy, with a piece of TiN sponge added before re-melting, was analyzed for nitrogen and the alloying elements on a line from the sponge material into the matrix to test the diffusion profile of all the elements along the line. The relationship of the nitrogen and alloying elements is seen as we move from the porous TiN sponge, with no other elements than nitrogen and titanium, to the alpha zone with decreasing nitrogen and increasing aluminum and vanadium, to the matrix with no detectable nitrogen and the approximate alloy composition of six weight percent aluminum and four weight percent vanadium.

We are now investigating oxygen, another alpha-stabilizing element with its own set of problems in titanium alloys. Many samples of both industrial defect analysis and our own experimental products have proven the value of this method.

References

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4. G. F. Bastin and H. J. M. Heijligers, "Quantitative Electron-Probe Microanalysis of Very Light Elements," Microbeam Analysis—1985, 1:

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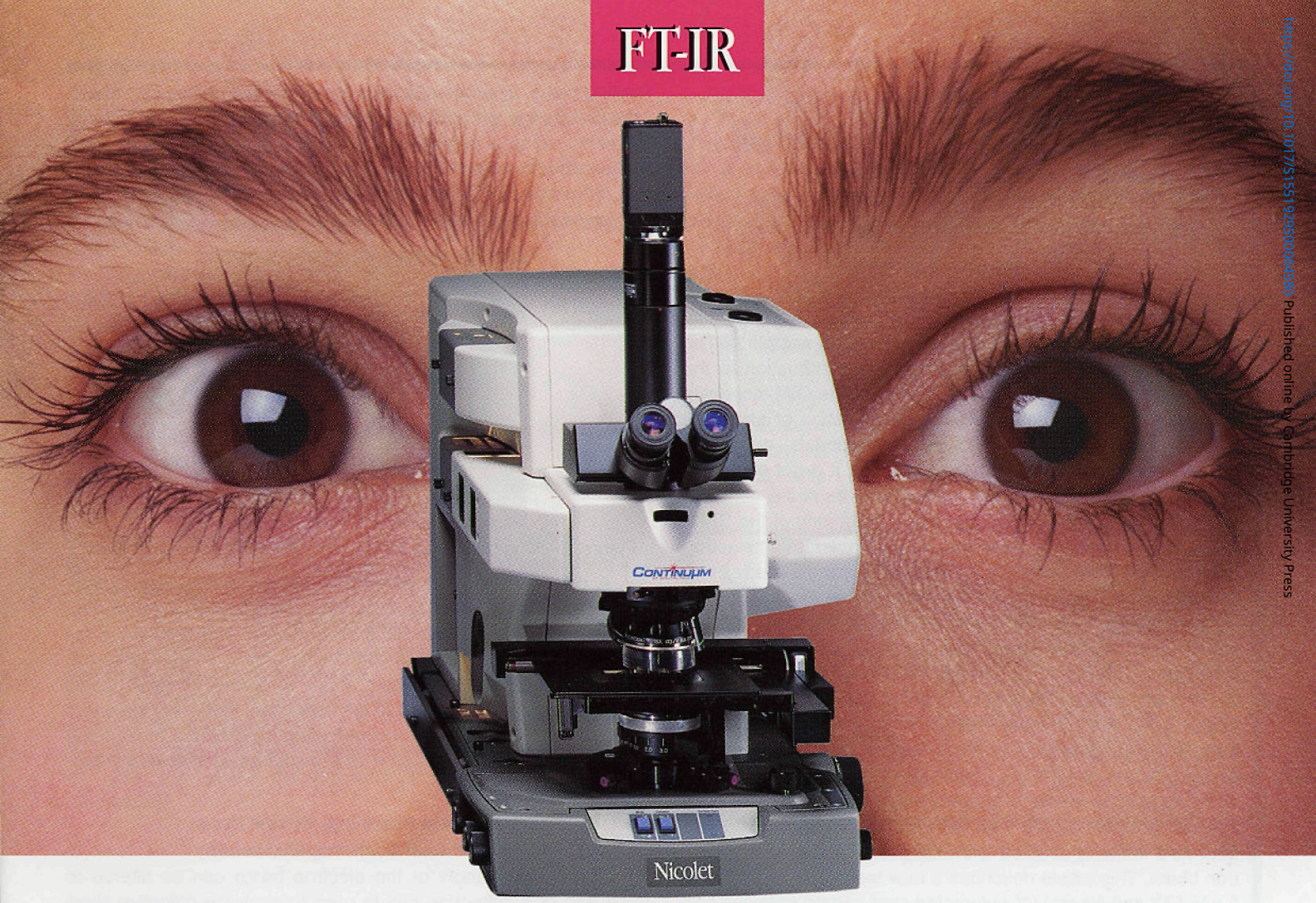

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