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The effects of nitrogen additions to a cobalt–chromium surgical implant alloy

Part 2 *Mechanical properties*

A. J. DEMPSEY, R. M. PILLIAR, G. C. WEATHERLY
Department of Metallurgy and Materials Science, University of Toronto, Toronto M5S 1A4, Canada

T. KILNER
Mathematics, Physics and Computer Science Department, Ryerson Polytechnical Institute, 350 Victoria Street, Toronto M5B 2K3, Canada

The efficacy of adding nitrogen to a Co–Cr surgical implant alloy in order to improve tensile and fatigue properties has been investigated. Using the heat treatments described in Part 1 of this study, the tensile properties of specimens with nominally 0.14, 0.19, 0.21 and 0.33 wt% carbon were evaluated in air at room temperature. The fatigue testing consisted of a rotating beam fatigue test at room temperature in air, at a frequency of 10 Hz. The results of the mechanical tests indicated that interstitial nitrogen additions to low carbon alloys (nominally 0.14 wt% carbon) increased the yield strength while maintaining good ductility. However, this beneficial effect was not apparent for the material tested in fatigue, possibly because of the overriding influence of inherent flaws within the heat treated testpieces.

1. Introduction

In Part 1 of this study [1] the feasibility of making nitrogen additions to a cobalt based surgical implant alloy was evaluated, and it was found that under certain conditions a significant amount of nitrogen entered the alloy in solution. The increase in solubility of nitrogen in the alloy compared to the solubility of nitrogen in pure cobalt was attributed to the presence of chromium which has a strong affinity for nitrogen.

When present in solution the nitrogen might act as a solid solution strengthener, resulting in an increase in the yield strength of the material. A distribution of fine nitride precipitates would also be expected to increase the static mechanical strength of the alloy, but this could be accompanied by a reduction in ductility to an unacceptable value.

Surface treatment is a well-established method of improving the wear and fatigue resistance of steels. A necessary requirement for the nucleation of a fatigue crack is general or localized plastic flow; if plastic flow is impeded, so is the initiation process. Surface hardening techniques which result in increased yield stress will retard plastic flow. These include flame-hardening and induction-hardening. In addition to surface hardening techniques, compressive stresses can be induced at the material surface. Techniques which result in residual surface compressive stresses are carburizing, nitriding, and shot-peening [2]. The introduction of nitrogen to the F75-76 alloy, even within a limited surface zone as suggested by our studies [1], may affect fatigue response either through increased yield strength of the surface region, or through the introduction of a surface compressive stress, or a combination of both. The purpose of this study was to investigate the effect of nitrogen on mechanical properties of this cast surgical implant alloy with specific attention to tensile and fatigue characteristics.

2. Experimental procedure

2.1. Tensile testing

The tensile samples all met the chemical requirements for the ASTM F75-76 specification and had four different initial nominal carbon contents: 0.33, 0.21, 0.19 and 0.14 wt%. The standard tensile specimens were cast, conforming to ASTM E8-69 specifications for threaded-end tensile specimens of 6.25 mm diameter. The samples were treated in bundles of four, one sample of each carbon content. The heat treatments used are the same as in Part 1 of this study [1] and are summarized in Table I. Apart from the PC heat treatment, all heat treatments were done in a SiC element horizontal tube furnace with temperature control of $\pm 5^{\circ}$ C. After heat treating, the specimens were tested in air using an Instron mechanical testing machine at a crosshead speed of 2 mm min^{-1}.

2.2. Fatigue testing

Fatigue testing was performed on the F75-76 alloy using a rotating beam fatigue testing machine (R = fatigue ratio = -1). All tests were conducted in air at a frequency of 10 Hz. The testpieces were of the continuous radius waisted type, the dimensions of which are shown in Fig. 1. Two stress levels were used: 250 and 325 MPa. Fatigue tests were performed on the

TABLE I Summary of heat treatments

PC	1295° C, 3 h (vacuum); cooled $1° C min^{-1}$ to 1200° C; 1200° C, 0.5 h; gas quench
PC + AMM	PC followed by: 1220° C, 3 h in ammonia; 1220° C, 1 h in argon; water quench
PC + HT − AMM	PC followed by: 1300° C, 2 h, ammonia; cooled $1° C min^{-1}$ to 1220° C; 1220° C, 1 h; water quench
PC + ESA	PC followed by: 1195° C, 48 h, argon; water quench
PC + 48AMM	PC followed by: 1195° C, 48 h, ammonia; water quench
PC + 48FG	PC followed by: 1195° C, 48 h forming gas; water quench

Co–Cr alloy in five conditions:

1. low carbon, after PC heat treatment
2. high carbon, after PC heat treatment
3. low carbon, PC and 4.5 h in a nitrogen-containing atmosphere
4. high carbon, PC and 4.5 h in a nitrogen-containing atmosphere
5. low carbon, PC and 24 h in a nitrogen-containing atmosphere.

The bars that were heat treated in a nitrogen-containing atmosphere were machined to approximate dimensions and then heat treated. The nitrogen heat treatments were carried out in a vertical tube furnace described in Part 1 of this study [1]. The atmosphere was a mixture of argon and forming gas selected to have a nitrogen content of approximately 25%. All the nitrogen heat treatments were followed by a water quench. These heat treatments caused warpage of the specimens to the extent that they could not be tested: therefore, machining after the heat treatment was performed to true the ends of the specimens with respect to the central waisted region. The specimens that were not heat treated in the vertical furnace were machined to finished dimensions after the PC heat treatment.

The surfaces of all specimens were prepared in a similar fashion. Initially the waisted section was ground by hand while rotating in a drill press (with 240 and 400 grit paper). Following this process the specimens were further ground by hand in the longitudinal direction with 600 grit paper until all the grinding marks appeared to be parallel to the long axis of the specimen at 20 × magnification.

3. Results
3.1. Tensile stress
The results of the tensile tests and the associated carbon and nitrogen contents of the alloys are summarized in Tables II and III. Carbon was included in

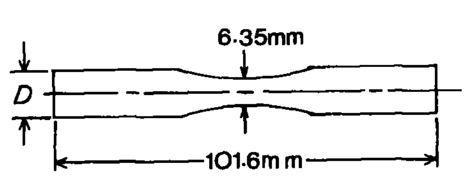

Figure 1 Dimensions of rotating beam fatigue testpiece. D = 12.07, 11.4 or 11.05 mm.

this analysis because of its strengthening role established in the testing on the variable carbon tensile samples [3]. The results are divided into four groups based on the nominal carbon content of the alloy prior to heat treatment. Table III compares the mechanical properties after each heat treatment to the material in the PC condition.

The PC + 48AMM heat treatment resulted in a large increase in interstitial content. With the exception of the 0.33 wt % C material, the elongation to fracture was increased, the 0.2% YS (yield strength) increased or remained the same, and the ultimate tensile strength (UTS) increased compared to the material after the PC heat treatment.

The forming gas heat treatment (PC + 48FG) consistently resulted in a reduced elongation to fracture, increased 0.2% yield strength, and decreased ultimate tensile strength, compared to the PC material.

The decrease in total carbon + nitrogen contents for the short time heat treatments (PC + AMM, PC + HT-AMM and PC + ESA) suggested that decarburization of the samples may have occurred. Consequently, significant changes in mechanical properties were not observed.

3.2. Fatigue testing
The tests performed at 325 MPa indicated that there was no improvement of the fatigue strength for the nitrogen-treated testpieces compared to the testpieces which received only the PC heat treatment. The data obtained in this work is in the range of fatigue data obtained for the Co-base alloy by our previous studies [4, 5] (Fig. 2). However, presentation of the fatigue data on a single S–N plot may be misleading. The mode of failure for the rotating beam tests fell into two categories: a macroscopic crack developed which resulted in sufficient deflection of the load arm to cause the test machine to shut down, or plastic deformation of the testpiece occurred to the extent that the machine shut down. The plastic deformation was not accompanied by the appearance of a macroscopic crack, nor were any cracks detected when the testpieces were sectioned. Instead, lines of concentrated slip were observed near the testpiece surface (Fig. 3). Typically, test cessation due to plastic deformation occurred for the low carbon testpieces which were not heat treated in a nitrogen-containing atmosphere or for those treated for 4.5 h. This did not occur for three of the four low carbon testpieces which were nitrogen-treated for 24 h.

The fatigue fracture surfaces of failed rotating beam testpieces exhibited a similar morphology to fatigue fracture surfaces of Co–Cr–Mo alloys observed by several other investigators [6–8]. The initiation region exhibited a series of flat facets inclined to the axis of loading (Fig. 4). A transition to the Stage 2 fracture mode was indicated by the presence of striation-like features and macroscopic crack growth perpendicular to the loading axis (Fig. 5).

4. Discussion
4.1. Tensile testing
The initial concern, and the reason for reducing the

TABLE II Mechanical properties of heat-treated cobalt-base alloy specimens. (To convert from weight p.p.m. to atomic p.p.m. multiply by 4.8 for carbon and 4.12 for nitrogen)

Alloy (nominal wt % C)	Heat treatment	Weight p.p.m. carbon	Weight p.p.m. nitrogen	Elongation (%)	0.2% YS (MPa)	UTS (MPa)
0.33	PC	3313	73	7.4	510	710
	PC + AMM	2708	364	14.3	540	670
	PC + HT − AMM	2813	437	10.5	490	710
	PC + ESA*	2646	73	5.0	480	670
	PC + 48AMM*	1563	1541	13.4	450	700
	PC + 48FG*	2188	2791	2.4	525	610
0.21	PC	2167	243	6.7	490	630
	PC + AMM	2313	1092	10.6	540	760
	PC + HT − AMM	2125	777	7.7	520	700
	PC + ESA*	1563	461	9.7	450	640
	PC + 48AMM*	1781	1614	15.4	505	805
	PC + 48FG*	1792	3447	4.3	540	605
0.19	PC	1896	534	13.6	460	710
	PC + AMM	1812	558	16.2	500	810
	PC + HT − AMM	2021	704	15.5	490	780
	PC + ESA*	1813	206	12.7	355	715
	PC + 48AMM*	2042	2172	18.8	460	765
	PC + 48FG*	1583	3544	6.6	535	635
0.14	PC	1417	437	14.9	390	710
	PC + AMM	1521	752	16.0	470	780
	PC + HT − AMM	1125	485	15.4	440	780
	PC + ESA*	1021	231	12.4	330	715
	PC + 48AMM*	1583	1954	19.1	510	860
	PC + 48FG*	1500	3568	12.5	525	685

*Represents the average of two tests.

starting carbon content of the alloy (from the typical value of 0.25 wt %), was the loss of ductility when this material was porous-coated at a sintering temperature of 1300° C. The decreased ductility of this material was due to the formation of extensive grain boundary precipitates [9]. The results of the PC + 48AMM and PC + 48FG heat treatments clearly showed that by nitrogen additions, it is possible to increase the 0.2% YS and the UTS of a low carbon content Co-base alloy to the extent that these properties are comparable to the 0.33 wt % C alloy in the PC condition.

The PC + 48AMM heat treatment resulted in an advantageous combination of properties. The increased nitrogen content improved both the yield and ultimate tensile strength and elongation to fracture was larger than for the material in the PC condition in every

TABLE III Change in carbon + nitrogen content and change in mechanical properties relative to the material in the PC condition

Alloy (nominal wt % C)	Heat treatment	Weight p.p.m. C + N	Elongation (%)	0.2% YS (MPa)	UTS (MPa)
0.33	PC + AMM	−314	6.9	30	−40
	PC + HT − AMM	−136	3.1	−20	0
	PC + ESA*	−667	−2.4	−30	−40
	PC + 48AMM*	−282	6.0	−60	−10
	PC + 48FG*	1593	−5.0	15	−100
0.21	PC + AMM	995	3.9	50	130
	PC + HT − AMM	492	1.0	30	70
	PC + ESA*	−386	3.0	−40	10
	PC + 48AMM*	985	8.7	15	175
	PC + 48FG*	2829	−2.4	50	−25
0.19	PC + AMM	−59	2.6	40	100
	PC + HT − AMM	295	1.0	30	70
	PC + ESA*	−411	−0.9	−105	5
	PC + 48AMM*	1784	5.2	0	55
	PC + 48FG*	2697	−7.0	75	−75
0.14	PC + AMM	419	1.1	80	70
	PC + HT − AMM	−244	0.5	50	70
	PC + ESA*	−602	−2.5	−60	5
	PC + 48AMM*	1683	4.2	120	150
	PC + 48FG*	3232	−2.4	135	−25

*Represents the average of two tests.

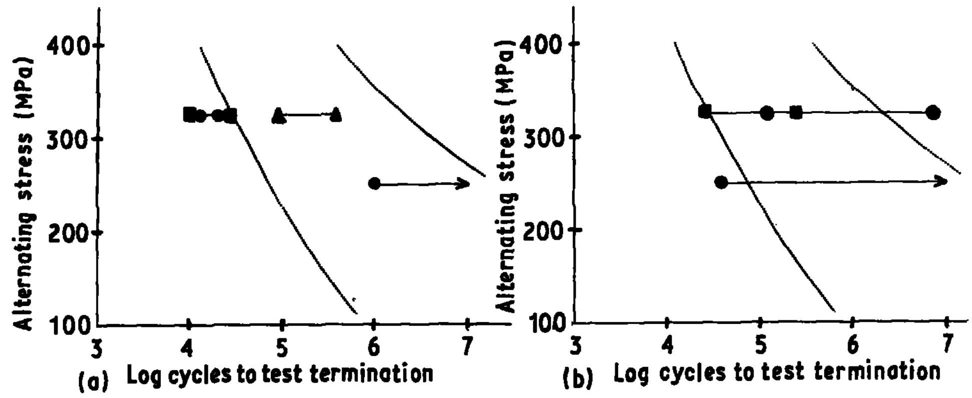

Figure 2 Summary of Co-base alloy fatigue data. The curved lines represent the range of results obtained in previous studies [4, 5] for the cobalt-base alloy for various material conditions. (●) PC heat treatment, (■) PC + 4.5 h nitrogen heat treatment, (▲) PC + 24 h nitrogen heat treatment. (a) Low C specimens, (b) high C specimens.

instance. The reduced nitrogen potential in this heat treatment atmosphere prevented the solid solubility for nitrogen in the Co-based alloy from being exceeded and as a result metallography did not reveal any precipitates. Although the PC + 48FG heat treatment results in increased yield strength, this increase is accompanied by a loss of ductility for all carbon contents relative to the material in the PC condition (Table III). Metallographic examination showed the reason for the decrease in elongation to fracture. All samples which were treated in forming gas had a second phase along the grain boundaries (Fig. 6) identified in Part 1 of this study as beta chromium nitride and chromium carbonitride.

4.2. Fatigue testing

4.2.1. High carbon content alloy

The results of the rotating beam fatigue tests indicated that there was no improvement of the fatigue life of the high carbon content alloy after a 4.5 h nitrogen heat treatment. It appears that any solid solution strengthening, due to the presence of an increased amount of nitrogen in the alloy, is outweighed by the solutionizing or decarburizing effect of the heat treatment. Both these effects could cause carbides to dissolve so that fatigue as well as static tensile properties do not increase.

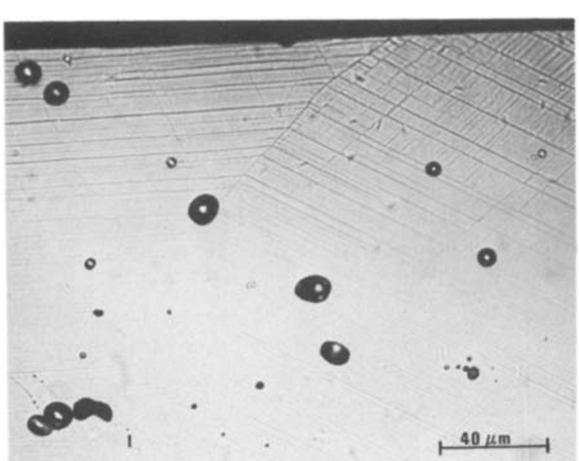

Figure 3 Surface of rotating beam fatigue testpiece after test termination.

4.2.2. Low carbon content alloy

The low carbon content alloy has a homogeneous microstructure after being subjected to the PC and the PC followed by nitrogen heat treatments. Unlike the high carbon alloy, very little grain boundary attack occurs when the structure is electrolytically etched (Fig. 3) which suggests that little if any second phase particles are present in the matrix or at the grain boundaries. After test termination the examination of the microstructure of low carbon testpieces, cycled at 325 MPa, revealed regions of concentrated slip (Fig. 3). The presence of extensive plastic strain explains the absence of a macroscopic fatigue crack at the specimen surface when the fatigue test was terminated. The presence of a fatigue crack for the testpieces which were run at 250 MPa may be the result of intense dislocation activity at a structural heterogeneity. The stress was insufficient to mobilize large numbers of dislocations (unlike the situation at 325 MPa) and hence crack, initiation occurred in the

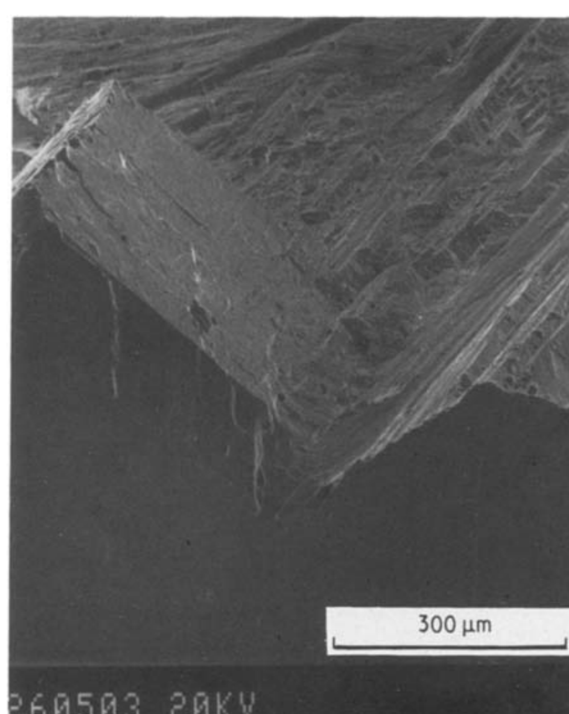

Figure 4 Initiation region of a failed rotating beam testpiece.

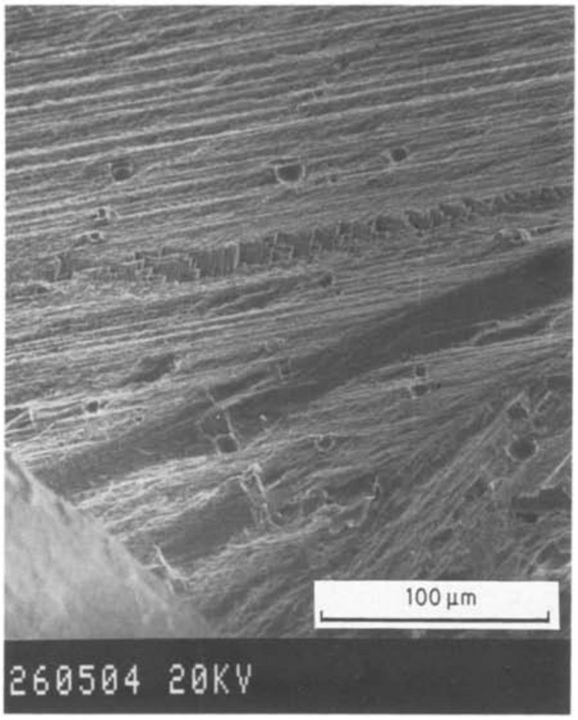

Figure 5 Core of a failed rotating beam fatigue testpiece.

vicinity of a stress concentrator such as a shrinkage pore. The 24 h nitrogen heat treatment caused three of the four testpieces tested at 325 MPa to exhibit a macroscopic fatigue crack at the material surface. This result agrees with the tensile tests which suggest that nitrogen acts as a solid solution strengthener. As a result of the increased amount of nitrogen present in the material, dislocation motion is more difficult and hence, the yield strength of the material is increased.

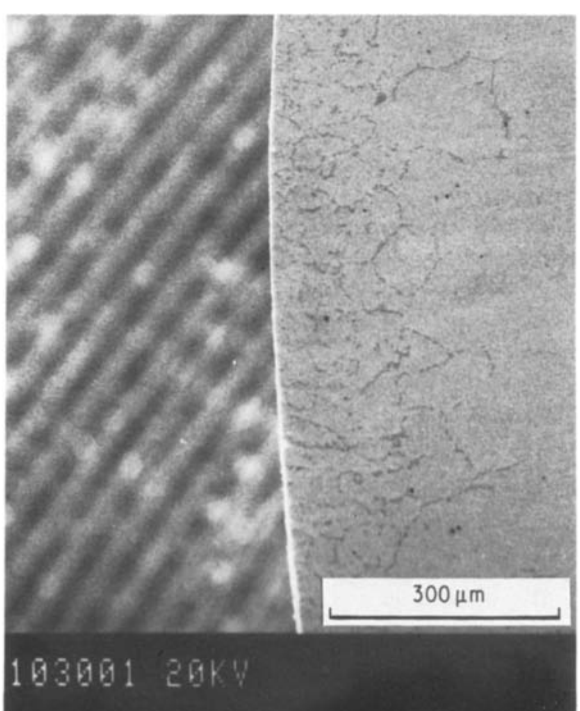

Figure 6 Sample treated in 85% nitrogen atmosphere for 24 h showing chromium nitrides and carbonitrides along grain boundaries at the surface.

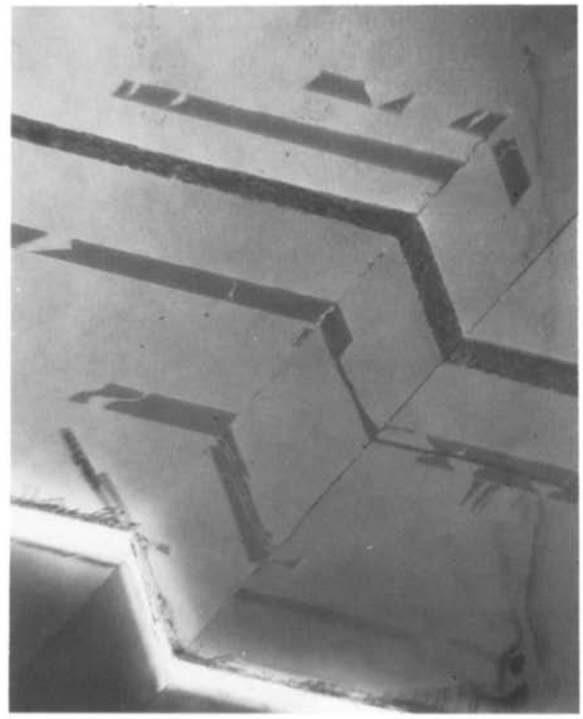

Figure 7 TEM micrograph of crack in foil parallel to twin and stacking faults. Specimen treated in an 85% nitrogen atmosphere for 24 h at 1200° C and water quenched.

Because dislocation motion is impeded, the microstructure of the failed testpiece does not show any significant evidence of plastic strain as was the case for the low carbon material which received only the PC heat treatment (Fig. 3). The difficulty of initiating strain in the matrix forces dislocation motion to occur at a region of structural weakness. Several foils prepared for TEM work exhibited cracks which ran along twin boundaries parallel to stacking faults (Fig. 7). This may indicate easy cleavage at twin boundaries where a thin layer of effectively h c p material exists. Gell *et al.* [10] cite coherent annealing twin boundaries as a location of crack initiation in wrought nickel-base superalloys at room temperature.

Tensile tests represent an averaging of the material properties over the section of a given testpiece. By comparison, fatigue can be looked upon as a single event phenomenon where the benefit of a strengthening by nitrogen additiόns is negated by the presence of regions of structural weakness (e.g. porosity, twin boundaries) inherent to the cast material.

5. Conclusions

In the first part of this study it was shown that through the correct choice of heat treatment parameters it is possible to introduce a significant amount of nitrogen into the Co–Cr alloy as an interstitial solute. The introduction of nitrogen had the desired effect of increasing the yield strength of the low carbon content alloy while maintaining its good ductility (19%). However, the addition of nitrogen as an interstitial solute did not improve the fatigue strength of the low carbon alloy to a level that made it superior to the high carbon content alloy which had received the PC heat treatment.

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