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Evaluation of Oxidation and Fatigue Damage of Retrieved Crossfire Polyethylene Acetabular Cups

By Barbara H. Currier, MChE, John H. Currier, MS, Michael B. Mayor, MD, Kimberly A. Lyford, BA, John P. Collier, DE, and Douglas W. Van Citters, PhD

Investigation performed at the Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire

Background: Crossfire cross-linked polyethylene is produced differently from other cross-linked polyethylene materials; a below-melt-temperature annealing process is used with the goal of avoiding compromised mechanical properties. The present study was performed to evaluate retrieved Crossfire acetabular cups to determine whether they had oxidized and to what extent oxidation might have influenced their clinical performance.

Methods: Eleven acetabular cups were received at retrieval and a twelfth acetabular cup was received two years post-retrieval over a period of four years. None were retrieved because of polyethylene wear or fatigue. The cups had been in vivo from 0.1 to 5.3 years. Each was examined visually, clinical fatigue damage was rated, and oxidation was measured with use of Fourier transform infrared spectroscopy.

Results: The cups exhibited oxidation that varied with its location on the cup: the oxidation value was generally low on the articular surface but more than an order of magnitude higher value on the rim. Maximum rim oxidation correlated significantly with the time in vivo (Spearman rho = 0.734, p = 0.010). Oxidation was identified visually by a white band in thin sections on the rim of seven of the cups and on the articular surface of one of these seven cups. Six of the seven cups also exhibited clinical fatigue damage. Eight of the twelve cups exhibited evidence of impingement or dislocation.

Conclusions: Acetabular cups made of Crossfire polyethylene oxidized to a measurable degree. The oxidation-related reduction of polyethylene mechanical properties was sufficient to allow the fatigue damage seen in these retrieved cups.

Clinical Relevance: The oxidation measured in acetabular cups made of Crossfire polyethylene makes them susceptible to fatigue after as little as three years in service.

The link between polyethylene wear debris and osteolysis[1] is well established and has led orthopaedic manufacturers to introduce cross-linked polyethylenes that can reduce wear rates to near zero[2]. Most currently marketed cross-linked materials are irradiated with a dose of 50 to 100 kGy, followed by a melting process to eliminate free radicals. The combined processes lower mechanical properties to near American Society for Testing and Materials (ASTM) minima for surgical implants[2-4], requiring careful design considerations to ensure satisfactory clinical performance.

In contrast, Crossfire cross-linked polyethylene acetabular cups (Stryker Orthopaedics, Mahwah, New Jersey) receive two doses of gamma irradiation. The initial cross-linking dose (75 kGy), which produces free radicals in the polyethylene in addition to cross-links[2,5], is followed by below-melt-temperature annealing. The goal of below-melt annealing is to avoid the reduction in mechanical properties that results from melting; however, a below-melt anneal does not quench all of the free radicals[3,6]. Sterilization of Crossfire components with standard gamma irradiation in oxygen-barrier packaging produces additional free radicals in the polyethylene. In a previously published study, the free-radical concentration in Crossfire polyethylene was found to be twice as high as that in standard gamma-barrier sterilized polyethylene[2].

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TABLE I Data on the Patients from Whom the Crossfire Cups Were Retrieved

Case	Time in Vivo *(yr)*	Reason for Retrieval	Gender	Body Mass Index*	Age* *(yr)*
1	0.1	Instability	M	21.3	76
2	0.3	Instability, lysis	M	22.2	66
11	0.4	Pain, acetabular fracture	F	21.8	63
3	1.1	Loosening	M	NA	55
6	2.0	Instability	F	NA	NA
4	2.6	Pain, loosening of femoral component	F	37.2	72
8	2.9	Instability	F	26.2	NA
5	3.3	Pain, proximal lysis around stem	F	32.8	71
7	3.3	Dislocation × 2	F	59.5	59
12	3.3	Pain, aseptic loosening	F	27.4	60
10	3.5	Loosening	F	29.9	60
9	5.3	Subsidence	M	25.8	58

*NA = not available.

Oxidation of gamma-sterilized-in-air polyethylene, initiated by radiation-induced free radicals, has been shown to result in a reduction in polyethylene mechanical properties[7] that is much greater than the reductions in mechanical properties due to cross-linking and remelting[2]. The concentration of free radicals in Crossfire polyethylene is higher than that in standard gamma-sterilized polyethylene[2]; therefore, Crossfire polyethylene has the potential for more rapid oxidation when it is exposed to oxygen or oxidizing species. We evaluated a group of retrieved Crossfire acetabular cups to determine whether the remaining free radicals oxidize and whether oxidation-related loss of polyethylene mechanical properties, combined with unintended rim-loading due to impingement or dislocation, could result in the fatigue damage seen in these retrieved cups.

Materials and Methods

Eleven Crossfire acetabular cups were received at retrieval and one cup was received two years post-retrieval from eight surgeons from five different institutions over a period of four years. Three of the cups had an elevated lip, and the remaining nine had a standard shape. After disinfection in formalin and drying, each retrieved cup was photographed and examined visually with use of a Nikon binocular dissecting microscope (Nikon, Tokyo, Japan) with a magnification factor of 10×. All of the cups were rated for clinical fatigue damage on a scale of 0 (none) to 3 (severe) on the basis of the retrieval analysis protocol originally developed by Hood et al.[8]. The focus was on pitting, cracking, and delamination, with 0 indicating no visible evidence of the particular mode of damage; 1, barely observable changes; 2, easily detected levels of change; and 3, severe changes, often implying a threat to the function of the implant (see Appendix).

Eight of the twelve acetabular cups in this series were retrieved after two years or more in vivo. Patient characteristics and reasons for retrieval are listed in Table I.

Sample Preparation and Fourier Transform Infrared Spectroscopy Analysis

The retrieved acetabular cups were cut with a band saw to expose a vertical cross section. Thin slices (approximately 200 μm thick) were removed parallel to the exposed cross section with use of a microtome (Jung, Heidelberg, Germany), as il-

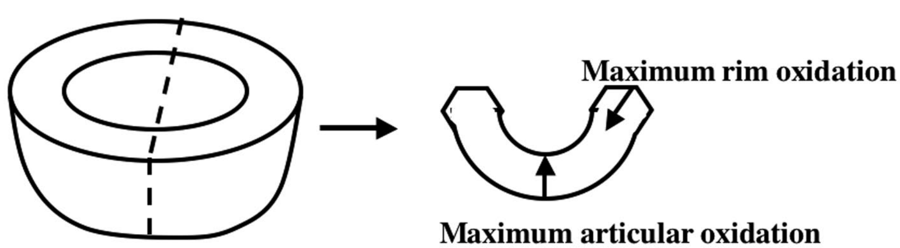

Fig. 1

Diagram illustrating the sample preparation technique for Fourier transform infrared spectroscopy analyses of retrieved Crossfire polyethylene acetabular cups.

TABLE II Effect of Cup-Lip Geometry, Evidence of Impingement, and Evidence of Dislocation on Clinical Fatigue Damage

Type of Clinical Fatigue Damage	Correlation with Cup-Lip Geometry		Correlation with Impingement		Correlation with Dislocation	
	Rho Value	P Value	Rho Value	P Value	Rho Value	P Value
Cracking	–0.034	0.918	–0.265	0.406	0.177	0.583
Delamination	–0.329	0.296	0.225	0.482	0.289	0.362

lustrated in Figure 1. These vertical cross sections were analyzed for oxidation with use of a Perkin-Elmer AutoIMAGE microscope attached to a Perkin-Elmer BXII Fourier transform infrared spectrometer (Norwalk, Connecticut). Ketone peak height ratio (1715 cm^{-1}/1370 cm^{-1}) was reported as an indication of the oxidation measured through the thickness of the acetabular cup and on the rim of the cup (Fig. 1).

The 1715 cm^{-1}/1370 cm^{-1} peak height ratio method of oxidation analysis was evaluated in an inter-laboratory study[9] and was found to be second only to the carbonyl area method in inter-laboratory reproducibility (mean uncertainty, 22% for the peak height ratio method and 16.5% for the carbonyl area method). The peak height ratio method was found to be statistically equivalent to the carbonyl area method in terms of intra-laboratory repeatability, and it addressed concerns stated in the ASTM standard for evaluating oxidation in surgical implants[10]. The appendix to this standard stated that the presence of biological residues (absorbed into polyethylene cups in vivo) complicated the use of the carbonyl area to determine the level of oxidation of retrieved implants. Use of the peak height ratio method for reporting oxidation of retrieved cups minimized the effect of absorbed species on measured oxidation. Oxidation values calculated with the peak height ratio method, with use of thin sections from retrieved Crossfire bearings, were correlated with those calculated with the carbonyl area method, and the relationship was reported to allow the reader to convert the reported oxidation values if desired (see Appendix).

Statistical Methods

Data regarding the retrieved Crossfire cups (the time in vivo, clinical fatigue damage ratings, and oxidation measurements) were not normally distributed. Therefore, a nonparametric correlation, Spearman rho, was used to evaluate the correlations among the data. The correlation coefficient and p value were reported for all correlations. The maximum oxidation was determined on the articular surface of each cup and on the rim of each cup. A paired t test was used to compare the mean measurements of the maximum articular surface oxidation and the maximum rim oxidation. The significance of relationships was evaluated with use of SPSS software (version 12; SPSS, Chicago, Illinois).

Results

None of the twelve acetabular cups were retrieved because of polyethylene wear or fatigue; however, six exhibited some level of clinical fatigue damage. None exhibited pitting, but four exhibited cracking and three exhibited delamination

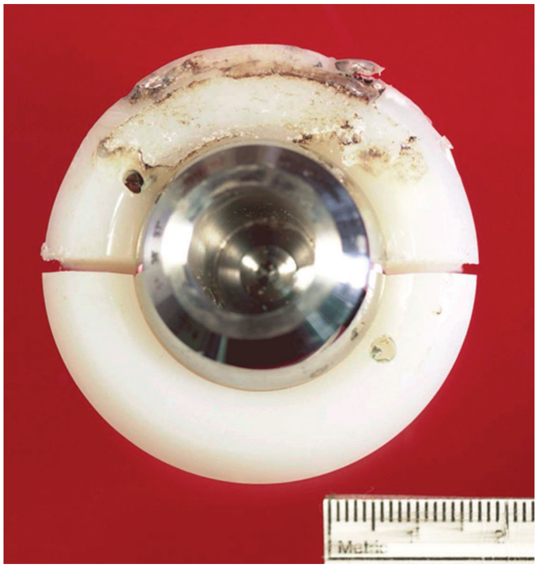

Fig. 2-A

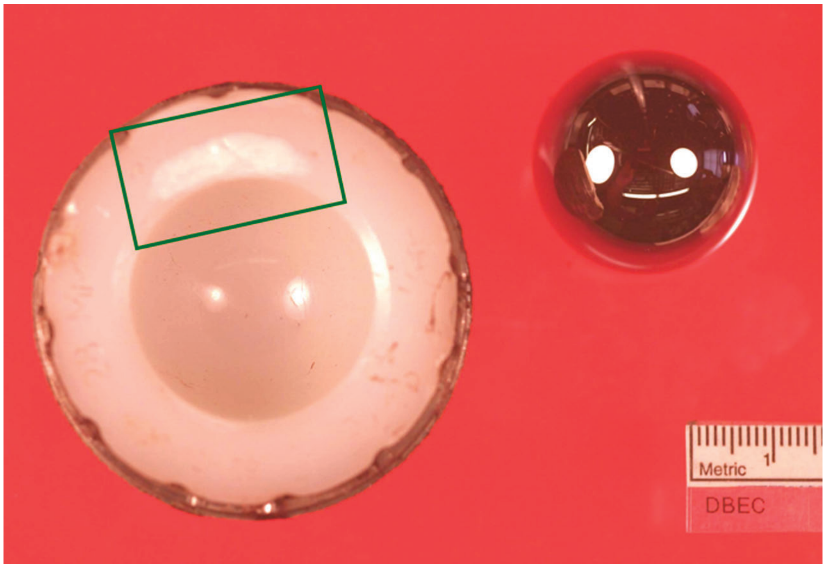

Fig. 2-B

Figs. 2-A and 2-B Retrieved Crossfire acetabular cups with fatigue damage in the form of rim delamination. **Fig. 2-A** Case 8. Severe delamination seen after 2.9 years in vivo. **Fig. 2-B** Case 12. Moderate delamination seen after 3.3 years in vivo.

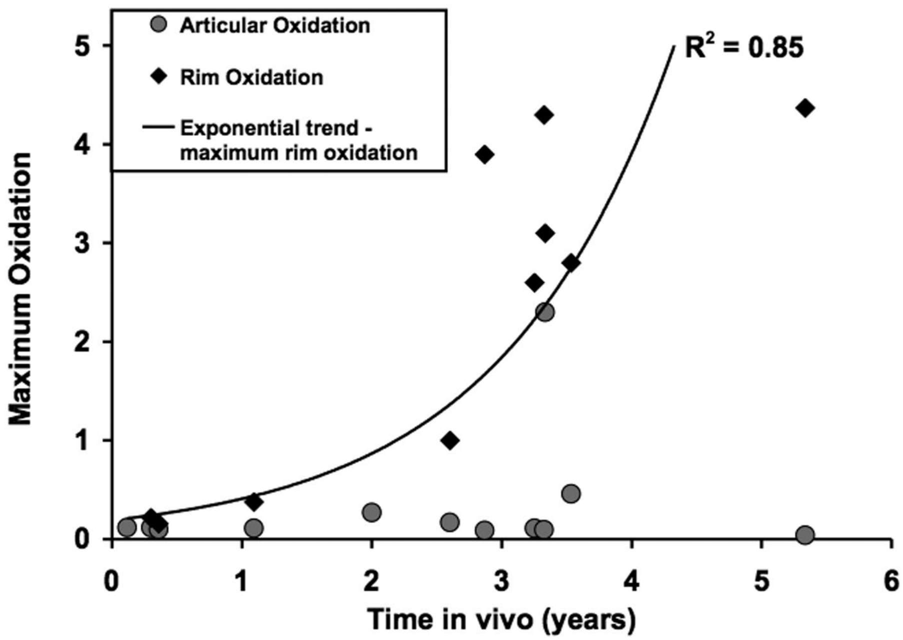

Fig. 3

Maximum oxidation measured on the articular surface (circles) of eleven Crossfire cups (the cup with two years of post-retrieval shelf time before analysis is excluded from this plot) and on the rim (diamonds) of ten Crossfire cups (rim oxidation was not measured in one cup) is shown versus time in vivo.

(one of these seven cups exhibiting both cracking and delamination). This fatigue damage was limited to the rim of the acetabular cups (Figs. 2-A and 2-B).

Five of the retrieved cups (all standard-rim cups) showed clear evidence of impingement. A sixth cup (Case 5, also with a standard rim) had some indications of impingement; however, because of severe damage to the cup from the retrieval process, this possible impingement could not be verified. Two of the five cups with clear evidence of impingement also showed evidence of dislocation. Three additional cups (two standard cups and one elevated-rim cup) showed evidence of dislocation without impingement. The geometry of the cup, evidence of impingement, and evidence of dislocation individually had a low correlation with the presence of clinical fatigue damage (Table II).

Measured oxidation varied with its location within each retrieved acetabular cup (Table III). The value for maximum articular oxidation was generally low (mean, 0.35 ± 0.66), with the exception of one cup with maximum articular oxidation of 2.3. Maximum articular oxidation did not appear to vary as a function of time in vivo (Spearman rho = –0.106, p = 0.743; Fig. 3). The mean maximum rim-oxidation measurement (2.38 ± 1.65) was more than an order of magnitude higher than the mean maximum articular oxidation. Paired-sample t tests showed low correlation between articular oxidation and rim oxidation (correlation coefficient = 0.035, p = 0.923) and a large difference (–2.03) between their means (p = 0.003).

Oxidation was frequently visually apparent as a white band on a thin section of a cup (Fig. 4). A white band was noted on the rim of seven of the twelve cups and on the articular surface of one of these seven cups (Table III). Six of the seven cups also exhibited clinical fatigue damage.

Delamination of the cup did not appear to correlate

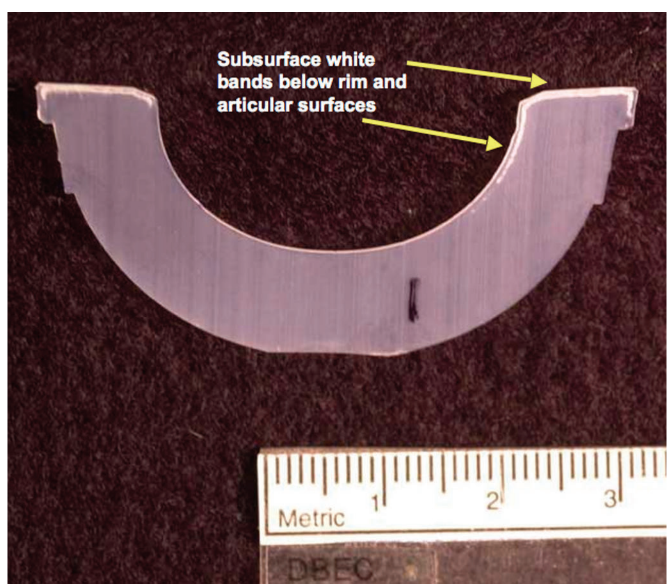

Fig. 4

Case 12. A thin section of a Crossfire acetabular cup retrieved after 3.3 years in vivo shows a subsurface white band on the rim and the articular surface.

TABLE III Maximum Measured Articular and Rim Oxidation and Clinical Damage of Retrieved Crossfire Cups

Case	Articular Oxidation	Rim Oxidation	White Band Presence	Impingement or Dislocation	Evidence of Fatigue
1	0.1	Not measured	None	Both	None
2	0.1	0.2	None	None	None
11	0.1	0.2	None	Dislocation	None
3	0.1	0.4	None	Impingement	None
6	0.3	3.4*	Rim*	Both	Delamination
4	0.2	1.0	None	None	None
8	0.1	3.9	Rim	Dislocation	Cracking, delamination
5	0.1	2.6	Rim	Possible impingement	None
7	0.1	4.3	Rim	Dislocation	Cracking
12	2.3	3.1	Articular and rim	Impingement	Delamination
10	0.5	2.8	Rim	None	Cracking
9	0.1	4.4	Rim	Impingement	Cracking

*This bearing was sent for analysis two years after retrieval. Oxidation values and the presence of a white band were influenced by this long time on the shelf before analysis. However, the clinical fatigue damage (severity-1 delamination) that this bearing exhibited suggests that this bearing had oxidation of >1.5 at the time of retrieval.

with time in vivo (Spearman rho = 0.102, p = 0.753), but rim cracking did appear to correlate with time in vivo (Spearman rho = 0.614, p = 0.034). Maximum rim oxidation appeared to increase with time in vivo (Spearman rho = 0.734, p = 0.010), a trend best described as exponential (R^2 = 0.85, Fig. 3). The maximum rim oxidation of these retrieved Crossfire cups was higher than the oxidation measured in shelf-aged, gamma-sterilized-in-air polyethylene (Fig. 5). The presence of the white band in thin sections of the retrieved Crossfire cups appeared to correlate with time in vivo

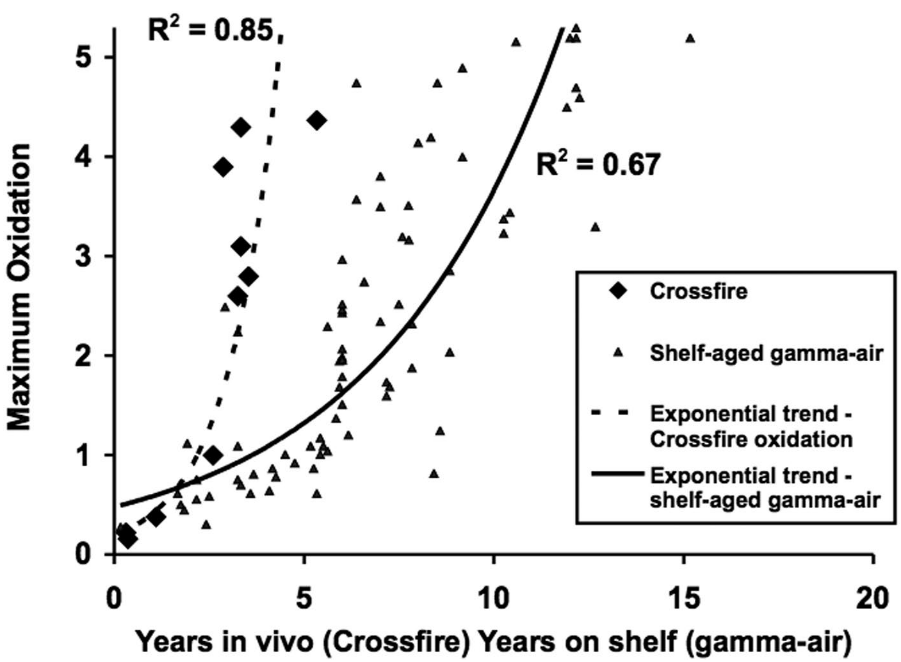

Fig. 5

Maximum oxidation measured on the rims of retrieved Crossfire cups (diamonds) is compared with the maximum oxidation measured in standard polyethylene inserts (triangles) that were shelf-aged after gamma sterilization in air.

(Spearman rho = 0.851, $p < 0.001$) and with the level of rim oxidation (Spearman rho = 0.853, p = 0.001). Cracking ratings also appeared to correlate with the rim oxidation level (Spearman rho = 0.704, p = 0.016). Delamination had a low correlation with oxidation alone (Spearman rho = 0.393, p = 0.232), with impingement alone (Spearman rho = 0.225, p = 0.482), and with dislocation alone (Spearman rho = 0.289, p = 0.362). However, delamination did appear to correlate with the combination of elevated oxidation (oxidation of >1.5) and unintended rim articulation (impingement and/or dislocation) (Spearman rho = 0.675, p = 0.016).

Discussion

This study addressed a two-part hypothesis: (1) Crossfire polyethylene is subject to oxidation because of its free radical content and (2) the reduced polyethylene mechanical properties, resulting from oxidation, were conducive to clinical fatigue damage. The twelve retrieved Crossfire cups available for evaluation confirmed both of these hypotheses.

All of the retrieved cups had measurable oxidation. Oxidation varied according to its location on the cup, as would be expected in cups exposed to the in vivo environment. Presumably, the metal shell and femoral head shielded parts of the polyethylene cup, preventing contact with oxidizing fluids or tissues. We believe that the rim of the cup oxidized many times faster than the articular surface because of its access to oxidizing fluids or tissues. The rate of this rim oxidation exceeded even the rate of shelf oxidation of never-implanted gamma-sterilized-in-air polyethylene.

The variability of oxidation within a cup and the maximum oxidation occurring on the cup rim were consistent with those reported in other published studies[11,12]. An earlier study of retrieved Crossfire acetabular cups demonstrated mechanical properties, characterized with use of small punch tests, that were reduced only minimally or not at all by the measured oxidation[12]. Those mechanical properties were measured in samples taken from worn and unworn areas of the articular surface. The articular surface of the cups in the present study showed minimal oxidation and would not be expected to have reduced mechanical properties. However, the seven cups in the present study that had rim oxidation values exceeding 1.5 would be expected to have severely reduced mechanical properties (ultimate tensile strength and ductility [elongation]) on the basis of earlier studies of the effect of oxidation on mechanical properties of clinically relevant polyethylene[13,14]. Those studies demonstrated that polyethylene with oxidation values of >1.5 had a 60% loss of tensile strength and an 80% loss of elongation compared with nonoxidized polyethylene, a combination that would be conducive to clinical fatigue damage, as seen in the retrieved Crossfire cups in our study. All of the cups with cracking and/or delamination in our study had measured oxidation values of >1.5.

Eight of the twelve retrieved cups in the present study exhibited definite evidence of impingement or dislocation. This unintended articulation could be expected to cause damage to the cup rims. However, only five of these eight cups exhibited clinical fatigue damage, and these five cups had maximum rim oxidation that exceeded 1.5.

Our findings suggest a chain of events leading to clinical fatigue damage. Neither rim cracking nor delamination occurred as a result of impingement or dislocation alone. Rather, rim cracking correlated with oxidation, suggesting that cracking could occur simply as a result of increased oxidation. Delamination, however, did not appear to correlate with oxidation alone. The three Crossfire cups with rim delamination had maximum rim oxidation of >1.5 combined with evidence of either impingement or dislocation, or both. We believe that the combination of measured oxidation of >1.5 (resulting in severely reduced strength and ductility) and cycles of stress (unintended rim articulation) was necessary to produce the delamination seen on the rims of these Crossfire cups.

In earlier studies of well-functioning Crossfire implants[15-17], radiographic analyses have shown substantially reduced wear rates compared with those of standard gamma-sterilized polyethylene. We did not address wear rates in the present study, but nothing in this series suggested unusual wear (head penetration) of the articular surface. The present study showed that stable, well-functioning Crossfire cups did not have rim delamination; however, eight of the twelve cups had evidence of dislocation or rim impingement. A published study demonstrated evidence of impingement in >50% of randomly selected retrieved cups[1]. We believe that the cup impingement in the present study resulted in rim delamination after less than three and one-half years in vivo because the oxidation of the cup rims had reached a level of >1.5. Presumably, the relatively rapid oxidation exhibited by these retrieved Crossfire cups resulted from the free radicals remaining in the polyethylene following cross-linking and sterilization by gamma irradiation.

Half of the retrieved cups in this study exhibited fatigue damage on their rim (loss of material through delamination and/or cracking). This fatigue damage after a short time in vivo (as little as three years in all but one case) raises concerns about debris generation by material removal through delamination and the potential for more serious cracking leading to rim separation.

New materials with a limited clinical history, including all types of highly cross-linked polyethylene, should be monitored carefully to ensure an effective performance in patients. This study of retrieved Crossfire acetabular cups demonstrated that Crossfire polyethylene oxidizes over time, changing its mechanical properties (ultimate tensile strength and ductility). The mechanical properties of Crossfire polyethylene after an average of three years in vivo were reduced compared with those of the newly implanted material as indicated by the oxidation levels that we measured. This reduction in mechanical properties can be expected to continue as oxidation increases over time in vivo. One effect of these reduced mechanical properties was demonstrated by the fatigue damage on the rims of the retrieved cups.

Appendix

eA Figures illustrating different severities of clinical fatigue damage as rated with the system used in this study and a figure showing the correlation between the carbonyl area and peak height ratio methods of calculating oxidation values are available with the electronic versions of this article, on our web site at jbjs.org (go to the article citation and click on "Supplementary Material") and on our quarterly CD-ROM (call our subscription department, at 781-449-9780, to order the CD-ROM). ■

Barbara H. Currier, MChE
John H. Currier, MS
Michael B. Mayor, MD
Kimberly A. Lyford, BA
John P. Collier, DE
Douglas W. Van Citters, PhD
Thayer School of Engineering, Dartmouth College, 8000 Cummings Hall, Hanover, NH 03755. E-mail address for B.H. Currier: barbara.h.currier@dartmouth.edu

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