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Evaluation of Oxinium (Oxidized Zr2.5Nb) Femoral Heads in Hip Endoprostheses—Case Report

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Abstract

Total hip arthroplasty (THA) is a widely performed and successful surgical treatment for degenerative joint disease. With increasing use in younger and more active patients, the demand for durable, biocompatible, and low-wear implant materials has grown. Oxidized zirconium (Oxinium, Zr2.5Nb) was introduced as a promising femoral head material, combining the strength of metal with the low-friction properties of ceramic. Despite encouraging early results, clinical reports have documented complications including head wear, especially after dislocation, and metallosis. We present the case of a 64-year-old male who underwent primary THA in 2009 and required revision in 2021 due to severe metallosis. Notably, no dislocation was observed that could explain the damage to the Oxinium head. Surface and subsurface analyses using X-ray photoelectron spectroscopy (XPS) and micro-indentation hardness testing revealed wear and deformation inconsistent with Oxinium's anticipated durability. These findings highlight the importance of the femoral head–polyethylene liner interface in implant longevity. Although Oxinium–XLPE articulations remain promising, risks such as damage to the femoral head, liner dislocation, impingement, and metallosis must be carefully considered. Surgical technique, liner placement, and locking mechanisms play critical roles in preventing failure. Further biomechanical and clinical studies are needed to optimize implant design and improve long-term outcomes.

Keywords: total hip arthroplasty; Oxinium; PE liner dislocation; wear; impingement

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1. Introduction

1.1. Hip Endoprosthesis

Orthopedic patients, such as those experiencing pain when engaging in daily activities, possibly because of arthritis, damage or sudden injury, may seek several types of treatment. This may include exercise therapy, patient education, weight reduction or even manual therapy. Treatment is coupled with pharmacological treatment with paracetamol and non-steroid anti-inflammatory drugs (NSAIDs) [1]. If such treatments are not effective, patients may seek a surgical relief for pain, such as total hip arthroplasty (THA). During this procedure, damaged sections of the hip joint are removed and replaced with hip endoprosthesis. The aim of the THA procedure is to reduce pain and improve the patient's mobility and quality of life [2]. During hip replacement surgery, the surgeon removes the diseased or necrotic tissue from the hip joint, including bone and cartilage. The head of the femur and acetabulum are replaced with artificial materials [3]. Prosthetic components may either be press fit into the bone, allowing it to grow around the prosthesis, or they may be cemented into the bone. The quality and strength of the patient's bone is a factor in choosing the right fixation method [4]. Additionally, prosthetic components may be made from several different materials, such as metal alloys and different ceramics. The materials prostheses are made of should be biocompatible and enable the long-term survivability of the implant [5].

1.2. Brief History of Hip Endoprosthesis Biomaterials

Biomaterials used in medical applications, such as total hip replacement endoprostheses, must meet certain specifications regarding their design and material constitution. This includes their sphericity, dimensional tolerances, and surface finish [6]. During in-body prosthesis motion, particle debris is formed due to the friction of articular surfaces. The possible generation of debris from such materials must be explored, as its presence can trigger an inflammatory response from the body's macrophages. This can result in the degradation of tissue surrounding the prosthesis (osteolysis) [7]. As an increasing number of younger and more active patients are receiving total hip and knee arthroplasties, there is an increasing necessity to fabricate materials with increased longevity. With these materials, we can expect reduced bone loss and improved wear [8].

The hip endoprosthesis is made of femoral and acetabular components. The femoral component is nowadays made of two parts: a metallic stem and a head. The acetabular component is made of a metal acetabular cup and an acetabular interface. The femoral stem is made of cobalt–chromium (CoCr) or titanium alloy, though in the past it was also made of stainless steel [9]. The material used in femoral heads was often CoCr alloy, which articulates against the acetabular component. The latter is made of a metal cup and an interface. Ultra-high-molecular-weight polyethylene (UHMWPE), the newer highly cross-linked polyethylene XLPE [10], or ceramic was used for the acetabular interface [9].

Lately, the development of prostheses has been largely targeted towards reducing friction between the femoral head and the acetabular interface, thus reducing the wear of articulating surfaces. Attempts to harden the femoral head's CoCr surface and improve the quality of the XLPE acetabular interface have been made but have shown limited success [11]. There were promising results regarding reducing polyethylene prosthesis wear with the use of alumina and zirconia ceramics as replacements for the metal femoral head in the 1990s. However, the usage of ceramic components remained limited because of the lower toughness of this material [12].

1.2.1. Ceramics in Hip Endoprostheses

Ceramic materials for THA began being used decades ago. The aim was to reduce friction with polyethylene and consequent surface wear. They proved successful, showing reduced osteolysis, as well as lower revision rates [13]. Generally, ceramic femur heads on ceramic acetabular interfaces have shown a lower wear rate compared to that of metal-on-polyethylene and ceramic-on-polyethylene. This helps increase the lifespan of the prosthesis and improves the patient's quality of life [14]. In the late 1970s, zirconia-toughened alumina (ZTA) was developed as Biolox delta, which has an aluminum oxide matrix consisting of approximately 80% alumina, 17% zirconia, and 3% strontium oxide [15–17]. Zirconia was added to increase the material strength and prevent the initiation and propagation of cracks. An additional toughening mechanism was created with the addition of strontium oxide, which forms platelet-type crystals to dissipate energy by deflecting cracks. Zirconia at up to 25 weight % was introduced into an alumina matrix, fabricating a composite material that showed increased flexural strength, fracture toughness, and fatigue resistance [18]. ZTA composite exhibits the more favourable crack resistance and toughness of zirconium, in addition to its excellent wear, chemical, and hydrothermal resistance [5].

1.2.2. Oxidized Zirconium Zr2.5Nb Alloy (Oxinium, OxZr)

At the end of the last century, a new material alternative for hip endoprosthesis was introduced. It consists of a metallic zirconium alloy, Zr2.5Nb, and a smooth articulating surface of oxidized zirconium (Oxinium, OxZr). It was meant to display the toughness of metal with the benefits of a ceramic surface [12]. In Oxinium prostheses, ceramic is not applied as a coating onto the metal, but rather a 4–5 μm thick ceramic-to-metal diffusion surface zone. It is fabricated through heat treatment of the metallic head in air at 500 °C. The reaction transforms zirconia into a durable, low-friction oxide on top of the metal head. The product is therefore a metallic head with an Oxinium ceramic surface. Because the head is still mainly metallic, it does not carry the same risk of fracture as a regular ceramic head [8,19]. In vitro studies have demonstrated that less particle debris is formed with Oxinium femoral heads (Figure 1) than with CoCr heads when articulating with XLPE [20]. Oxinium heads, therefore, offer the potential to reduce wear and consequently increase implant longevity [8].

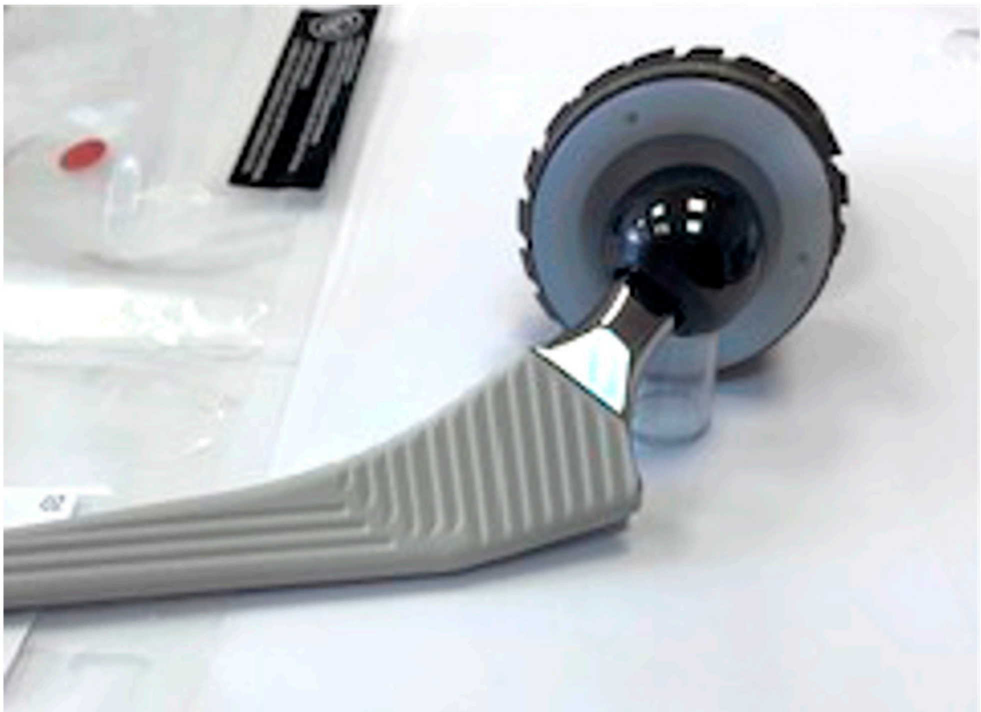

Figure 1. Components of the hip endoprosthesis with oxinium femoral head [Archive of the Orthopaedic Clinic of the University Medical Centre Ljubljana, Slovenia].

A schematic presentation of the formation of the Oxinium–ceramic-like diffusion layer is shown in Figure 2. After final shaping, the femoral heads (Zr2.5Nb alloy) undergo thermal oxidation in an air atmosphere at 500 °C. This process results in the formation of a ceramic oxide surface layer approximately 4–5 μm thick, underlain by an oxygen-enriched diffusion zone approximately 2 μm thick. Beneath this lies the ductile Zr2.5Nb metallic core, which provides toughness and structural integrity.

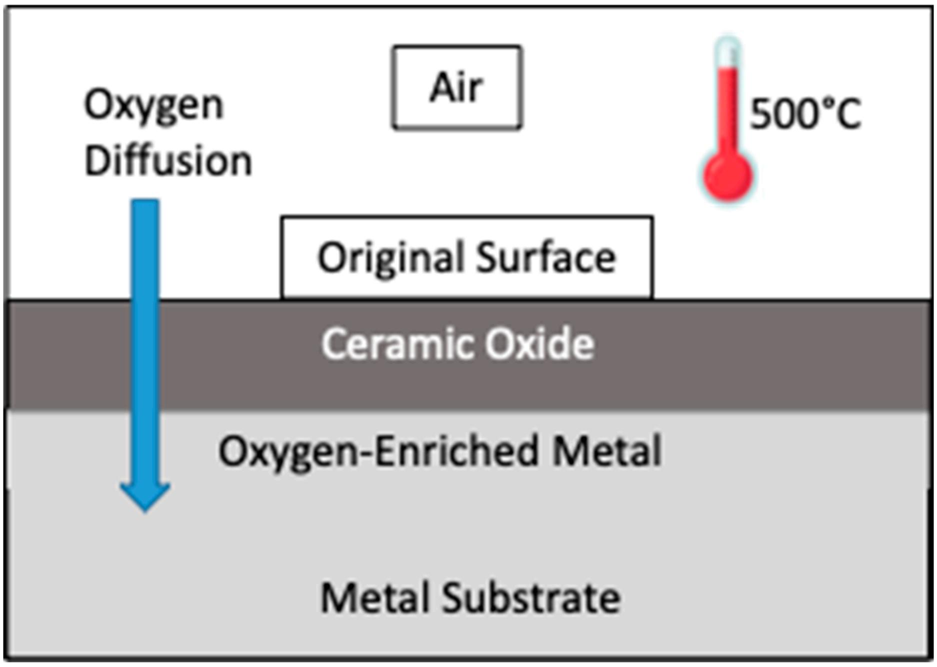

Figure 2. Schematic of Oxinium processing, adapted from Smith & Nephew [21].

1.3. Case Presentation

A 64-year-old male underwent total hip arthroplasty (THA) on 16 December 2009 (144 months prior to presentation) for hip dysplasia-induced osteoarthritis. The index procedure and subsequent rehabilitation were uneventful, following the standard protocol of the institution.

Approximately 140 months after the initial surgery, the patient sustained a fall while hiking, resulting in a contusion over the operated hip. At that time, radiographs revealed no evidence of fracture or prosthetic displacement. However, a polyethylene liner dislocation was noted, leading to direct articulation between the acetabular metal cup and the Oxinium femoral head. There was no polyethylene dislocation according to the radiographs, which would usually show this.

Unlike previously reported cases, in which major trauma or prosthetic dislocation was identified as the primary mechanism of Oxinium head damage, this patient had no endoprosthesis displacement and no gross dislocation of the prosthesis.

In the weeks following the incident, the patient reported progressively worsening pain localized to the greater trochanteric region. Shortly thereafter, he developed audible and palpable crepitus, which became increasingly pronounced. At 4 months post-injury, he presented with persistent, debilitating hip pain. Repeat radiographs demonstrated cranial migration of the femoral head within the acetabulum, consistent with advanced polyethylene liner wear and progressive prosthetic dysfunction.

In Figure 3, the X-ray demonstrates asymmetrical positioning of the femoral head within the acetabulum, suggesting possible component damage and/or wear. The direct articulation between the Oxinium femoral head and the Ti6Al4V acetabular cup has resulted in extensive metallosis around the prosthesis, visible as a characteristic cloud-like opacity. Metallic component wear is strongly suspected, since polyethylene liner wear would not be radiographically apparent other than through the observed head subluxation or asymmetry.

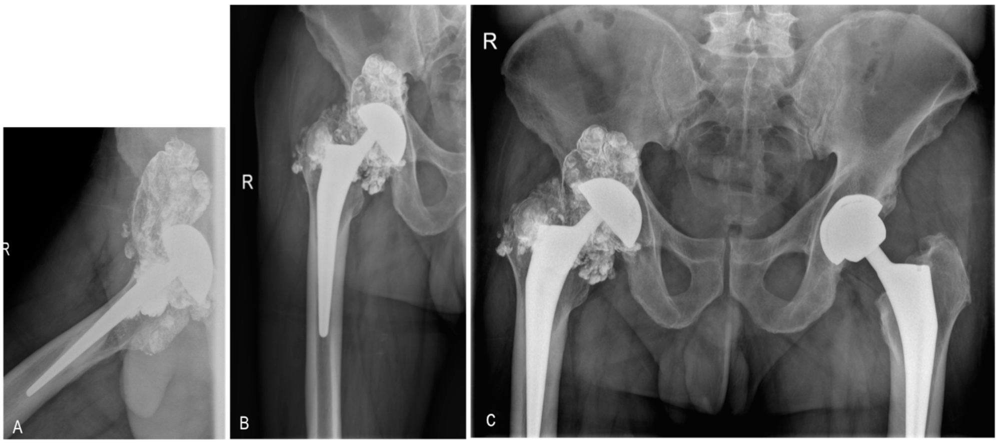

Figure 3. (**A**) Axial X-ray of the affected hip prosthesis. (**B**) Anteroposterior X-ray of the affected hip prosthesis. (**C**) X-ray of the whole pelvis showing right-affected hip prosthesis with extensive metallosis and normal left, non-affected hip. X-ray shows asymmetrical positioning of the femoral head within the acetabulum, suggesting damage and/or wear of the prosthetic components. There is evidence of direct contact between the Oxinium femoral head and the Ti6Al4V acetabular cup, which has resulted in extensive metallosis surrounding the prosthesis, visible as a cloud-like peri-prosthetic opacity. The findings indicate wear of metallic components, since polyethylene acetabular liner wear would not be radiographically visible apart from femoral head malposition. The Oxinium femoral head demonstrates severe wear, particularly involving the diffusion (ceramic) layer. Left hip/prosthesis: Symmetrical positioning of the components and femoral head with normal radiographic appearance.

In Figure 4, the X-ray after revision surgery demonstrates the symmetrical positioning of components. A lot of metallosis surrounding the soft tissues was removed; note the diminished peri-prosthetic opacity. All microbiology cultures and sonication of the explanted parts of the prothesis were negative. No histology of the removed soft tissue was performed.

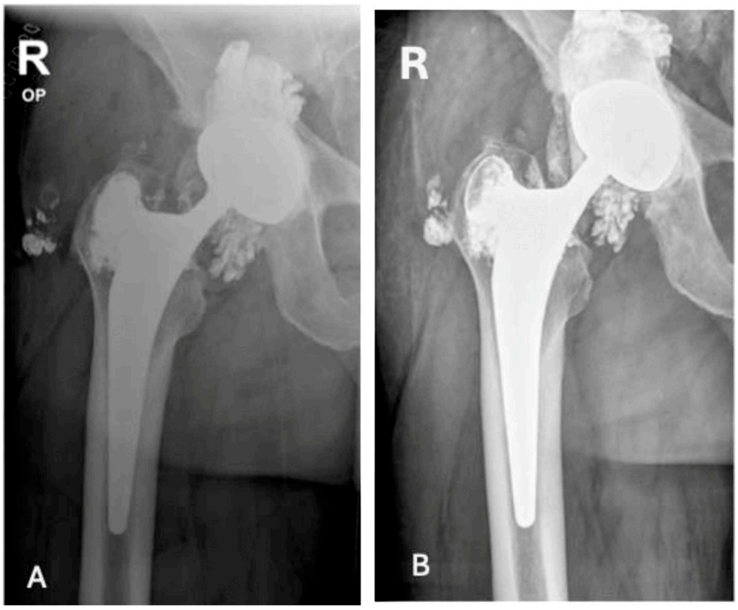

Figure 4. (**A**) 31 March 2021. X-ray after revision surgery. Extensive metallosis was found and mostly removed. Damaged femoral head, polyethylene, and acetabular cup were replaced. Proper symmetrical positioning of components was performed after femoral head and acetabular components were replaced. A lot of metal-infused soft tissues were removed—note the diminished cloud around the prothesis. (**B**) Routine X-ray at follow-up 2 months after surgery showed no dynamics.

The patient was satisfied with the surgical outcome and reported only slight limitations in range of motion (ROM). He works as a painter (residential and commercial), and occasionally experiences pain following heavy work or lifting heavy objects. No other complaints were reported.

2. Experimental Section

2.1. Materials and Methods

The initial implant was provided by Implantcast Eco Fit (Buxtehude, Germany).

2.1.1. Femoral Stem

Manufacturer/Provider: Implantcast (Buxtehude, Germany)
Model: Eco Fit
Size: 12.5 mm
Fixation: Cementless
Material: Ti6Al4V alloy (Titanium alloy)
Taper: 12/14 (for femoral head connection)

2.1.2. Femoral Head

Manufacturer: Smith & Nephew (Watford, UK)
Material: Oxinium (oxidized zirconium)
Diameter: 32 mm OD+4

2.1.3. Acetabular Cup

Manufacturer/Provider: Implantcast
Diameter: 52 mm
Fixation: Cementless
Material: Ti6Al4V alloy

2.1.4. Acetabular Inlay (Liner)

Manufacturer/Provider: Implantcast
Material: XLPE (cross-linked polyethylene)
Inner Diameter: 41 mm

2.1.5. New Oxinium Femoral Head (For Comparison) from the Same Manufacturer and of Same Material and Dimensions as Originally Implanted Femoral Head

Manufacturer: Smith & Nephew
Material: Oxinium (oxidized zirconium alloy: Zr2.5Nb)
Diameter: 32 mm OD+4
12/14 taper femoral head (for femoral head connection)
Zr2.5Nb

2.2. Sample Preparation

The retrieved Oxinium head samples were prepared for XPS and hardness measurements, and the new Oxinium head was processed in the same manner. The heads were sectioned into several parts using a Struers saw to obtain suitable samples for XPS analysis of the ceramic-like surface. The surface layer, approximately 4–5 μm thick, is extremely hard, whereas the retrieved worn Oxinium surface is slightly softer while the core material (Zr2.5Nb) is relatively soft. The metallographic sample was prepared using standard methods of grinding and polishing for hardness profile measurements.

2.3. Microbiological Analysis

All tissue samples collected during surgery were processed using a standard microbiological protocol using both PCR and standard cultures for aerobic and anaerobic bacteria; the presence of Cutibacterim Acnes was also observed. All implants removed during surgery were processed using sonication followed by microbiological analyses at the Institute for Microbiology, UMC Ljubljana, Slovenia. Both PCR and standard cultures for aerobic and anaerobic bacteria were used. Following the microbiological analysis, implants were cleaned and sterilized [22]. All microbiology findings were negative; no presence of bacteria was found.

2.4. XPS Surface Analysis

X-ray photoelectron spectroscopy (XPS) is a powerful analytical technique used to investigate the surface of materials, offering valuable insights into both their elemental and chemical composition. XPS is highly surface-sensitive, typically analyzing only the top ~10 nanometers of a sample. This exceptional surface specificity, combined with its ability to quantify surface chemistry, makes XPS an essential tool for material characterization and surface analysis. The main goal of XPS in our investigation was to obtain the surface composition of the 2–4 nm surface layer, identify the chemical oxidation states of elements/compounds and the distribution of elements at a depth of 0–40 nm in the new and retrieved Oxinium acetabular cups from the hip endoprosthesis.

2.5. Microindentation—Hardness Measurements

Hardness measurements of ceramic-like diffusion layer and worn surface were conducted through micro-indentation using the Fischerscope H100C instrument, Sindelfingen-Maichingen, Germany at a load of 0.005 N. The hardness profile of bulk material was measured using the Vickers hardness instrument Instron Tukon 2100B assembeled in Boston, MA, USA using loads of 1 N and 0.01 N.

3. Results

3.1. Hardness Measurements

The results of the hardness measurements of the ceramic-like diffusion layer vs. worn layer are presented (Figure 5).

Figure 5. (**A**) Sample of retrieved Oxinium femoral head HV from the worn surface region, 383 HV, and from the diffusion layer, 1159 HV, as shown in Figure 6. Red arrow indicates the location of measurements. (**B**) Cross-section of metallographic sample of retrieved Oxinium femoral head used for hardness measurement.

The results of the micro-indentation hardness measurements are given in Figure 6 for the retrieved Oxinium femoral head with the worn surface and the new unused Oxinium femoral head.

10 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	3591.81	5637.12	454.82	501.41	98.61	38.102	0.2442
	q	857.9	1740.99	141	144.68	19.42	8.277	0.0376
	s	690.9	1402.08	113.55	116.52	15.64	6.666	0.0303
	V/%	19.24	24.87	24.97	23.24	15.86	17.49	12.4
	Min.	2806.2	3929.6	316.6	362	85	30.04	0.211
	Max.	4408	7007.5	565.9	624.7	124.2	44.11	0.281
	R	1601.83	3077.93	249.29	262.67	39.22	14.071	0.0694
	R/%	44.6	54.6	54.81	52.39	39.78	36.93	28.44

50 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	3060.51	4118.91	331.87	382.4	107.76	30.922	0.6843
	q	296.15	294.26	23.78	29.56	23.46	5.186	0.0369
	s	238.5	236.97	19.15	23.81	18.89	4.177	0.0297
	V/%	7.79	5.75	5.77	6.23	17.53	13.51	4.35
	Min.	2748.1	3735	300.8	346.2	93.2	26.36	0.644
	Max.	3402.2	4354.4	350.9	410.5	139.6	36.7	0.725
	R	654.09	619.42	50.06	64.24	46.41	10.339	0.0816
	R/%	21.37	15.04	15.08	16.8	43.07	33.43	11.93

100 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	3370.65	4755.4	383.35	437.21	111.51	29.835	0.9517
	q	313.87	547.42	44.29	47.33	10.26	4.666	0.0477
	s	252.77	440.86	35.67	38.11	8.26	3.757	0.0384
	V/%	7.5	9.27	9.3	8.72	7.41	12.59	4.04
	Min.	3108.5	4212.2	339.4	393.1	100	26.54	0.909
	Max.	3655	5262.3	424.4	480.7	119.9	36.02	0.992
	R	546.54	1050.12	84.96	87.62	19.97	9.481	0.0829
	R/%	16.21	22.08	22.16	20.04	17.91	31.78	8.71

10 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	7100.4	12,843.58	1042.01	1093.15	170.75	60.067	0.155
	q	1123.48	2946.38	241.52	228.2	21.88	5.479	0.0162
	s	904.77	2372.82	194.51	183.78	17.62	4.412	0.0131
	V/%	12.74	18.47	18.67	16.81	10.32	7.35	8.44
	Min.	5999.2	9945	804.9	870.8	156.3	55.93	0.136
	Max.	8515.1	16,554.3	1346.5	1382.5	200.5	67.4	0.173
	R	2515.89	6609.29	541.63	511.77	44.24	11.47	0.0368
	R/%	35.43	51.46	51.98	46.82	25.91	19.09	23.73

50 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	7202.18	13,816.25	1121.52	1159.65	166.93	54.234	0.4194
	q	640.17	1420.77	116.46	112.76	16.32	3.637	0.0224
	s	515.55	1144.19	93.79	90.81	13.14	2.929	0.018
	V/%	7.16	8.28	8.36	7.83	7.87	5.4	4.3
	Min.	6429.2	11,965.2	969.8	1013.8	151.1	50.88	0.398
	Max.	7844.2	15,102.4	1227	1265.2	182.3	58.85	0.447
	R	1414.96	3137.21	257.21	251.36	31.15	7.973	0.0492
	R/%	19.65	22.71	22.93	21.68	18.66	14.7	11.73

100 mN	No. 1	HM	HUpl	HVpl	HV	EIT/(1-vs^2	nIT	hmaxI u
	n = 5	N/mm2	N/mm2			GPa	%	µm
	X	7834.92	16,514.87	1343.35	1345.37	169.23	56.822	0.5954
	q	704.01	1858.49	153.09	141.32	15.18	3.311	0.0296
	s	566.96	1496.7	123.29	113.81	12.22	2.667	0.0238
	V/%	7.24	9.06	9.18	8.46	7.22	4.69	4
	Min.	7259.3	14,888.5	1209.5	1224.7	159	53.33	0.561
	Max.	8684.9	18,538	1510.1	1504.7	189.4	60.8	0.62
	R	1425.6	3649.51	300.64	280	30.34	7.467	0.0599
	R/%	18.2	22.1	22.38	20.81	17.93	13.14	10.07

Figure 6. Hardness measurements of micro-indentation of ceramic-like worn and new Oxinium diffusion layer. Left table for the region with worn coating and right table for the region with Oxinium coating. The loads used were 0.01 N, 0.05 N, and 0.1 N. The yellow marked values of HV are the most significant.

The results of the hardness measurements of the bulk Zr2.5Nb metal alloy are given in Table 1. The loads used were 1 N and 0.01. The hardness profile of the bulk Zr2.5Nb is presented in Table 2.

Table 1. Hardness measurements of cross-sectioned oxidized bulk Zr2.5Nb using loads of 1 N and 0.01 N.

HV			
Base/HV 1	191	195	192
Base/HV 0.01	198	204	201
Edge/HV/0.01	262	252	267/279

Table 2. Hardness Profile on the bulk Zr2.5Nb oxinium metallographic cross section, HV Vickers at load 0.01 N.

Distance µm	HV 0.01
15	283
25	265
50	230
75	229
100	221
125	228
150	231
200	215
300	215
500	190

3.2. X-Ray Photoelectron Spectroscopy of Retrieved and New Oxinium Femoral Heads

XPS measurements were performed on the worn surface of the retrieved and new femoral heads, as indicated in Figure 7. The red arrows indicate the locations on the worn surface where the XPS analysis was performed on the retrieved femoral head and on the surface of the new Oxinium femoral head.

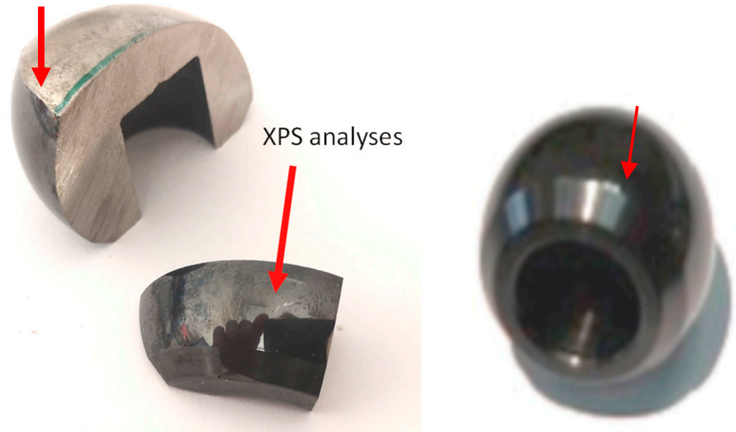

Figure 7. Red arrows indicate the locations where the XPS analysis was performed on worn and unworn surfaces of retrieved femoral head and new Oxinium femoral head for comparison studies.

The composition of the 2–4 nm surface layers of the new, undamaged and the retrieved, worn oxidized Zr2.5Nb diffusion layer is shown in Figure 8.

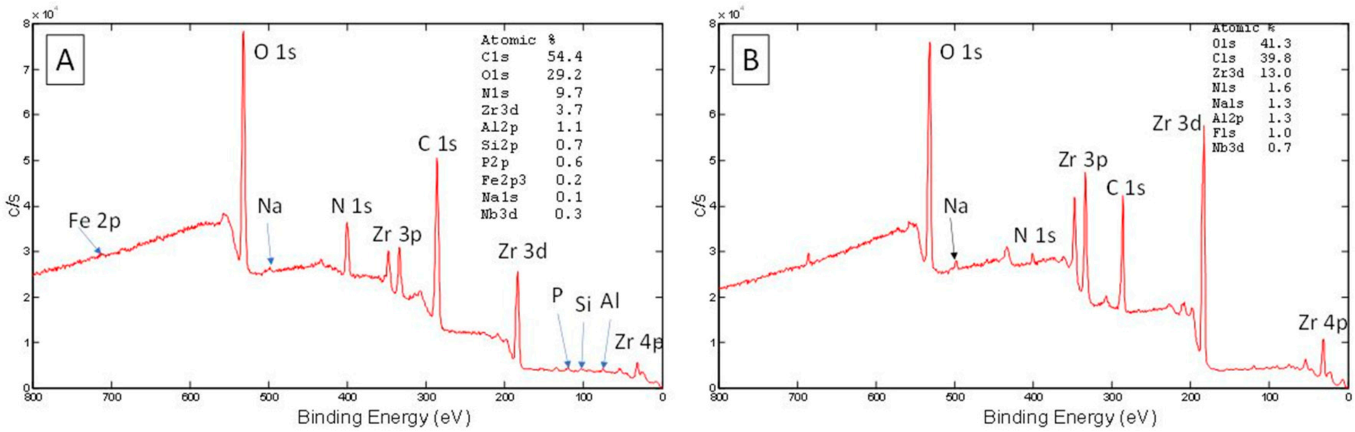

Figure 8. XPS spectra at the surface of (**A**) retrieved and (**B**) new Oxinium ceramic-like diffusion layer of femoral heads.

The XPS spectra at the surface of the retrieved and new Oxinium ceramic-like diffusion layer of the femoral heads are shown in Figure 8A,B. The surface composition, shown in Figure 8, of the retrieved femoral Oxinium head shows that the main phase is ZrO_2, and 0.3%Nb is present at the surface. Carbon is present, possibly from XLPE or contamination, and there is also 10% N, which may originate from soft tissue near the hip endoprostheses. We found Al 1.1, Si 0.7, Fe 0.2, P 0.6, and Na 0.1 (all in at.%). For comparison, we investigated the new unused femoral head and the surface composition was similar, with the main phase being ZrO_2 with 0.7 Nb; at the surface, C was present due to contamination and the elements present included Al 1.3; F1.0; and Na 1.3 (at.%). Figures A1–A3 in Appendix A show the high-energy resolution XPS spectra Zr 3d, Nb 3d, O 1s, C 1s, and Al 2p from the surface of the retrieved Oxinium femoral head. Figure A4 in Appendix A shows the XPS spectra O 1s and C 1s from the surface of a new Oxinium femoral head.

Figure 9 presents the XPS depth profile of surface layer beween 0–40 nm of the retrieved (Figure 9A) and new Oxinium femoral heads from the hip endoprostheses (Figure 9B).

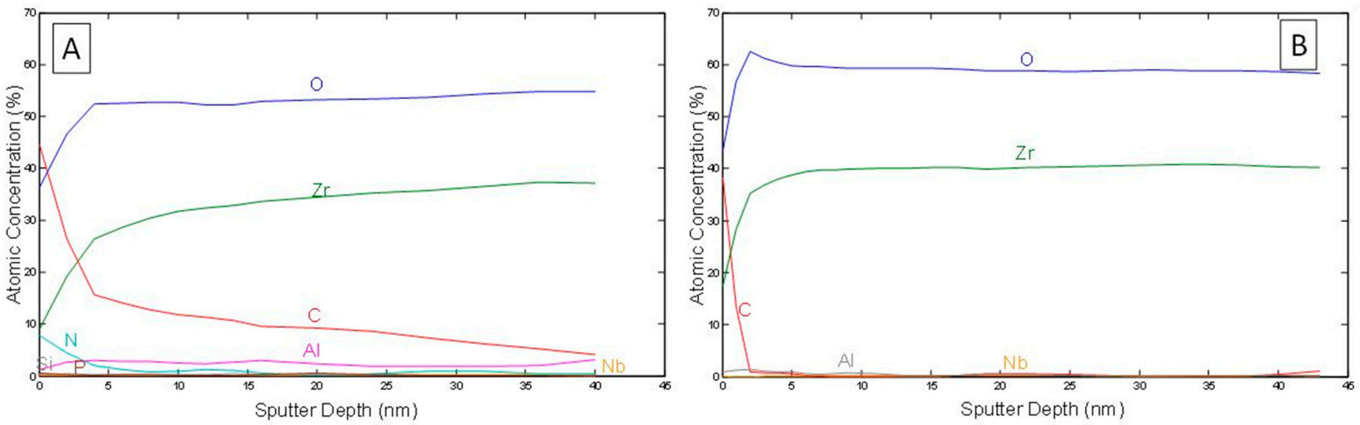

Figure 9. XPS depth profile of surface layer between 0–40 nm for oxidized Zr2.5Nb ceramic-like diffusion layer of retrieved (**A**) and new Oxinium femoral heads (**B**); ZrO_2 is the main phase in subsurface region, Al (~2–3 at.%) is present in subsurface region, and carbon decreases strongly from surface (only very thin contamination of 1–2 nm). Minor elements like Nb (0.2 at.%) are present in the coating.

The XPS spectra at a depth of 40 nm for the retrieved (Figure 10A) and new (Figure 10B) Oxinium femoral heads are shown in Figure 10.

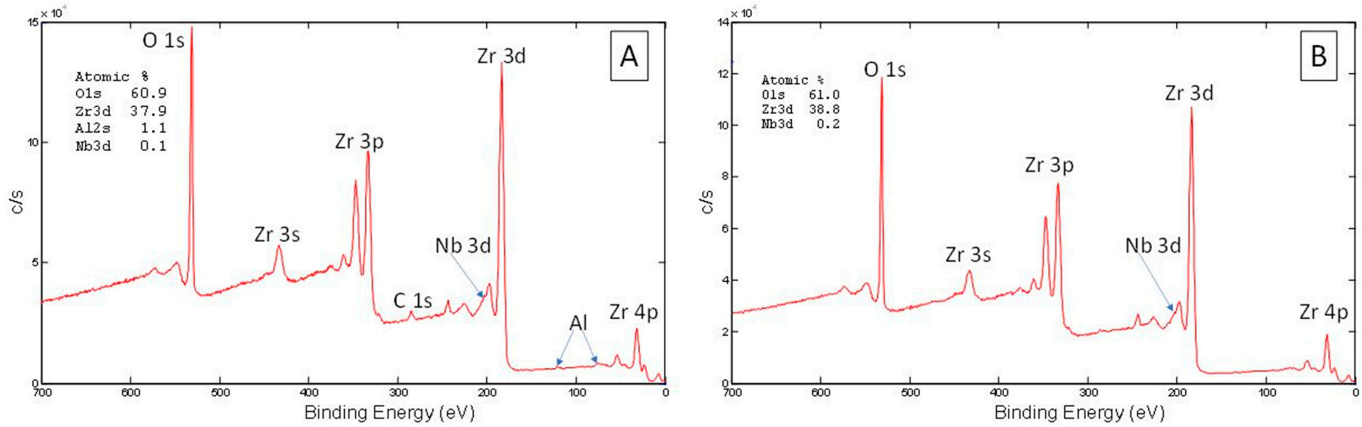

Figure 10. XPS spectra at a depth of 40 nm for retrieved (**A**) and (**B**) new Oxinium femoral heads from the diffusion ceramic-like layer.

Shown in Figure 10 are the XPS spectra presenting the surface compositions at a depth of 40 nm (Figure 10A) of the retrieved and (Figure 10B) new Oxinium femoral heads. The main phase of the composition at 40 nm is ZrO_2, 0.1 at.%, with Nb present and 1.1 at.% of Al.

Figure 10 shows the XPS spectra of the new Oxinium femoral head. ZrO_2 is the main phase in the subsurface region, with Al (~2–3 at.%) also present.

Carbon decreases strongly from the surface (only very thin contamination of 1–2 nm). Minor elements like Nb (0.2 at.%) are present in this layer.

The XPS analysis shows that the main phase on the surface and in the subsurface of the femoral heads is ZrO_2, where Zr is in the (4+) oxidation state. A small amount of Nb (0.1–0.3 at.%) in the Nb (5+) oxidation state is present in the surface region. Aluminum, Al, is also present in the surface region (1–3 at.%).

For the worn diffusion layer, the carbon on the surface may be related to interaction with the XLPE or from contamination.

For the new Oxinium head, the carbon surface layer is very thin (1–2 nm), and this is due to contamination.

A significant amount of nitrogen (10 at.%) is present on the surface of the retrieved femoral head (with worn Oxinium), probably due to soft tissue. Other elements are also present on the surface, like Fe, P, Si, and Na, on the worn coating. On the new Oxinium femoral head, the elements O, C, Zr, and Nb, and traces of Al and F are present.

4. Discussion

Several authors have reported that dislocated Oxinium femoral heads can undergo rapid, accelerated wear, potentially resulting in catastrophic implant failure [10,20,23–25]. Although Oxinium is reported to be twice as hard as cobalt–chromium (CoCr) on femoral heads [24], the underlying substrate is significantly softer, as demonstrated by Kop et al. [26] and corroborated by our own hardness measurements. These findings confirm a very hard ceramic-like oxide surface layer over a relatively soft metallic core.

In our patient, no major trauma or dislocation occurred, so we suppose that either mild dislocation occurred, which could explain the damage to the femoral head, or dislocation of the XLPE liner occurred and direct contact between the femoral head and metallic part of the acetabulum was made. This sort of event is the most common cause of damage to Oxinium femoral heads and rapid damage to artificial joints. It is our stipulation that despite adherence to standard diagnostic protocols, the dislocation of the polyethylene acetabular liner went undetected after the patient's fall, with no discernible clinical or radiological consequences for 140 months following the primary total hip arthroplasty (THA). This delay likely contributed to the progressive mechanical damage. Although Oxinium femoral heads offer a superior surface hardness to that offered by their CoCr counterparts, their clinical performance is critically dependent on the integrity of the polyethylene liner and its interface with the head. Damage or dissociation of the liner can lead to direct articulation between the femoral head and the acetabular cup, accelerating the wear and deformation of the Oxinium surface.

It is well established that polyethylene wear, particularly at the nanoscale, can result in "polyethylene disease," marked by the release of ultra-high-molecular-weight polyethylene (UHMWPE) particles. These nano-sized particles can trigger adverse local tissue reactions, including pseudotumor formation and osteolysis. To address this, highly cross-linked polyethylene (XLPE) enhanced with vitamin E has been developed, demonstrating improved oxidative stability and significantly greater wear resistance compared to conventional UHMWPE.

Multiple case reports support the notion that damaged Oxinium implants can fail prematurely. Ozden et al. described three patients who underwent revision surgery 3–7 years after their initial THA with Oxinium femoral heads. These patients, who had been asymptomatic initially, presented with pain, squeaking, or a shattering-glass sound during ambulation, and limited hip movement. Revision surgery revealed broken ceramic liners, severe deformation of the Oxinium heads, and tissue metallosis, although the metal femoral stems remained stable [23]. Similarly, Frye et al. documented eccentric positioning and deformation of Oxinium heads, polyethylene liner dissociation, and visible wear debris in patients with comparable symptoms prior to revision [25].

Jaffe et al. further demonstrated that damaged Oxinium heads exhibit a 50-fold increase in wear rate compared to their undamaged counterparts, particularly after contact with the metallic acetabular shell during dislocation or similar high-stress events [10]. These findings raise concerns about the reliability of Oxinium heads in patients with a higher risk of dislocation, challenging the perceived benefits of improved wear performance and prolonged implant longevity.

Additional case studies reinforce these concerns. Tribe et al. reported a patient who, after a dislocation episode, developed pain, instability, and squeaking in the hip. Revision revealed a cracked and displaced polyethylene liner, extensive metallosis, and severe edge wear on the Oxinium femoral head [10]. Likewise, Gibbon et al. described a unique case in which a fractured trochanteric fixation wire, following multiple dislocations, migrated into the acetabular cup and caused macroscopic damage to the Oxinium head. Once the hard oxide surface was compromised, the softer underlying alloy experienced rapid wear, resulting in severe tissue staining and implant degradation [10,10,27].

Common to all these cases is major trauma or dislocation of femoral head, which is not the case in our patient. These cases collectively demonstrate that while Oxinium heads may offer theoretical advantages in terms of surface hardness and wear resistance, their actual performance is highly contingent upon maintaining the structural integrity of surrounding components. Once compromised, Oxinium heads can degrade rapidly, generating particulate debris and leading to osteolysis, tissue reaction, and poor patient outcomes.

5. Conclusions

While in vitro studies have highlighted Oxinium as a promising prosthetic material with reduced surface friction, lower wear rates, and decreased debris formation—making them particularly advantageous for younger and more active patients—clinical reports have revealed significant limitations.

Numerous case reports have documented severe wear of the Oxinium ceramic-like surface following mechanical damage, often related to joint dislocation or contact with foreign objects. Patients frequently reported audible symptoms such as squeaking or a "glass-shattering" sound prior to revision surgery. In such cases, revision was invariably necessary due to accelerated implant degradation and surrounding tissue damage. All of these reports and clinical findings have made the use of Oxinium heads much less likely or common than was projected at the time.

Our XPS analysis confirms that the Oxinium surface is approximately twice as hard as that of cobalt–chromium (CoCr) femoral heads, and that the ceramic-like diffusion layer provides excellent properties initially. However, their critical weakness appears to be the interface between the Oxinium head and the highly cross-linked polyethylene (XLPE) liner. While this interface shows potential, further biomechanical and clinical studies are needed to optimize implant design, enhance durability, and improve surgical protocols to reduce the risk of catastrophic wear and failure.

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Institutional Review Board Statement: The study was conducted in accordance with the Declaration of Helsinki and approved by the Institutional Review Board (protocol code KME RS (Case No. 0120-121/2023/6)) (date of approval 14 November 2023) for studies involving humans.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

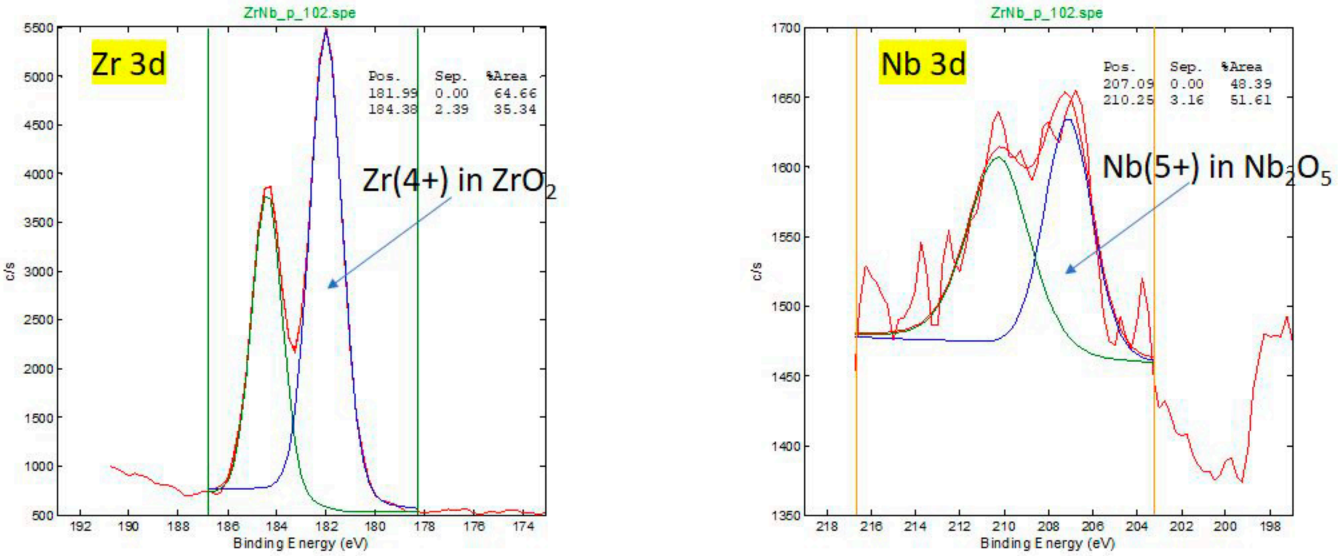

Figure A1. HR (high-resolution) XPS spectra for oxidation states of Zr and Nb of retrieved Oxinium femoral head. On the surface, Zr is in 4+ oxidation state in ZrO_2 and Nb is in 5+ oxidation state in Nb_2O_5.

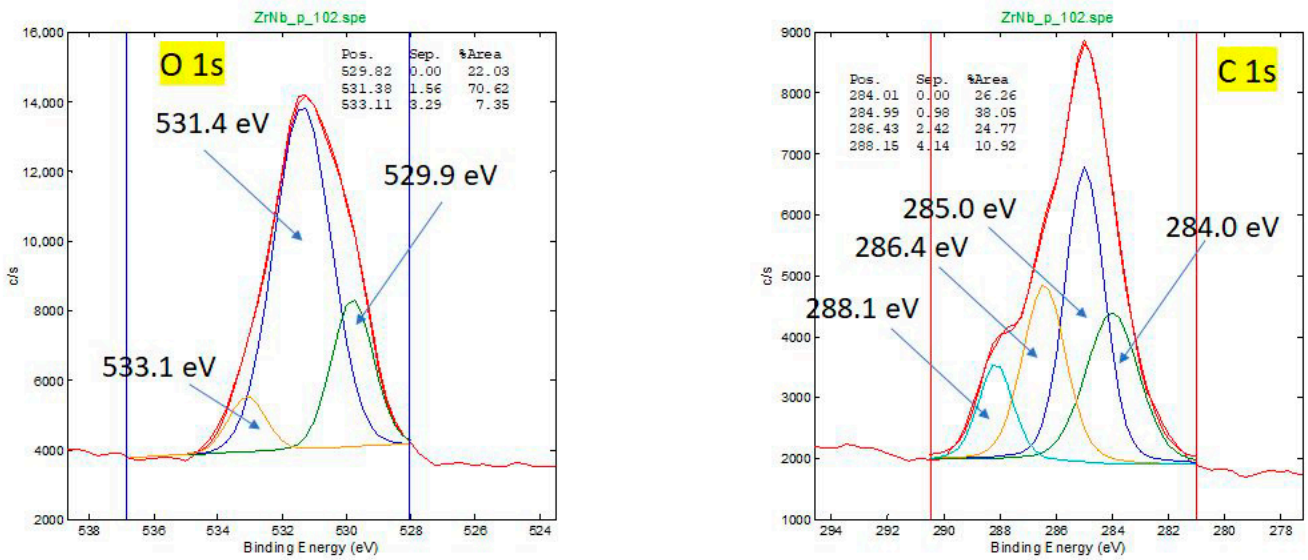

Figure A2. HR XPS spectra for oxidation states of O and C for retrieved Oxinium femoral head. Different oxidation states of O and C atoms on surface (oxides, polymer, contamination CO_2 adsorption).

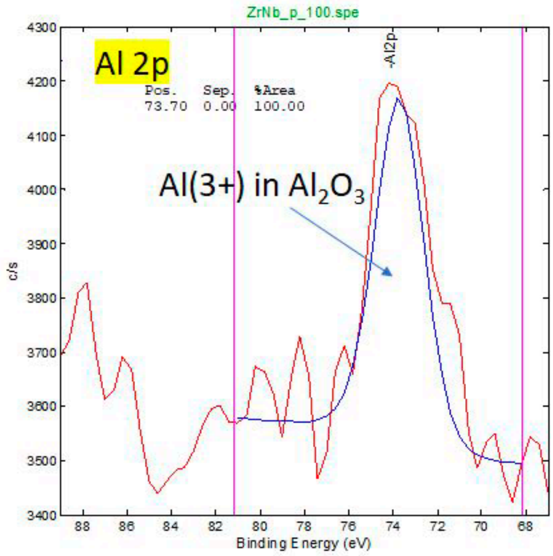

Figure A3. HR XPS spectra for oxidation states of Al for retrieved Oxinium femoral head. On the surface, Al is in 3+ oxidation state in Al_2O_3.

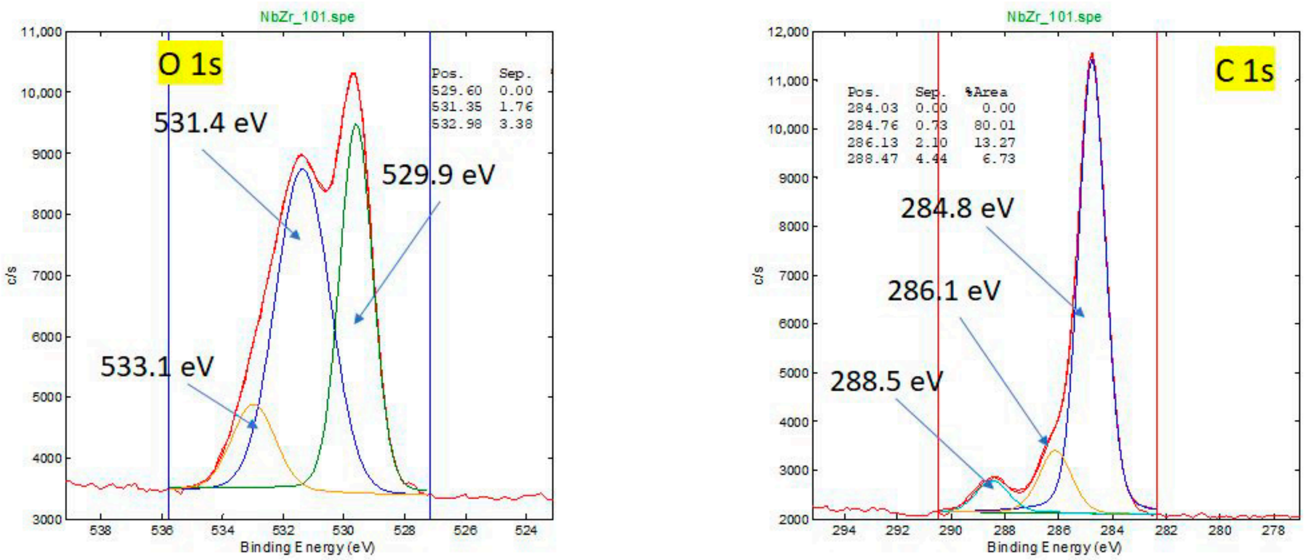

Figure A4. HR XPS spectra for oxidation states of O and C for new Oxinium femoral head.

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