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Wear properties of Co–Cr–Mo–N plasma-melted surgical implant alloys

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Abstract

This paper examines the feasibility of using metal-on-metal bearings to reduce the wear debris which commonly occurs in UHMWPE (ultra-high molecular weight polyethylene) joint materials in knee replacements. HPPM (high pressure plasma melting) was used to make high nitrogen Co–Cr–Mo implant alloys. The melted ingots were subsequently hot-forged and heat-treated. Sub-size specimens were used to evaluate tensile strength and wear properties. Experimental results indicated that the highest nitrogen content of ingots observed in this study was 0.288 wt.%, presenting better tensile and wear properties than those of specimens with less nitrogen. Homogenization treatment can further improve the wear resistance and ductility of the alloys.

Keywords: Plasma; Co–Cr–Mo surgical implant alloys; High nitrogen content; Mechanical properties; Wear properties

1. Introduction

Total knee joint replacements have improved the quality of life of people suffering from rheumatoid arthritis, bone cancer, trauma or bone fracture.

However, many recent researches have demonstrated that the release of wear debris was due to severe wearing of UHMWPE (ultra-high molecular weight polyethylene) between the patella and femur head.

Wear debris has been reported to induce osteolysis, causing patients to undergo prostheses several years after the first operation. Therefore, a study to reduce the problem of metal wear is urgently needed.

Using metal-on-metal bearings is an alternative to reduce the wear debris generated from UHMWPE in the total joint replacement; the concept was introduced in the 1960s and involves implants such as the Thompson, McKee-Farrar, Sivash, and Muller prostheses. However, the success of those implants was probably limited by their poor implant design and initial surface properties.

Metal-on-metal bearings have recently performed well in total hip prostheses. McCalden et al.'s [1] analysis of the components retrieved from metal-on-metal parings after extended service periods revealed a highly polished surface with minimal scratches, suggesting relatively low volumetric wear. Cobalt based alloys are preferred for use in metal-on-metal combinations due to their superior wear resistance to that of titanium alloys.

Two main cobalt-based alloys are widely employed in orthopaedic implant applications, namely cast Co–Cr–Mo alloys (ASTM F-75) and wrought Co–Cr–W–Ni alloys (ASTM F-90). A third alloy (ASTM F-562), known as MP35N, has also been used.

Several studies have investigated the effect of nitrogen additions on the strength of cast Co–Cr–Mo alloys. Cohen et al. [2] demonstrated that intragranular carbon-nitride precipitates could enhance the yield strength of the alloy. Kilner et al. [3] and Dempsey et al. [4] indicated that nitrogen diffused into the interstices of the γ-phase could increase the yield strength without compromising the ductility.

This study seeks to use a metal composition of low-carbon wrought Co–Cr–Mo–N alloys, which is similar to the metal femur component to reduce the wear problems of joint contact surfaces by alloy design and processing with nitrogen plasma arc melting.

The relationship among melting conditions, nitrogen addition, and mechanical strength will be discussed, as well as wear performances.

2. Experimental procedure

(a) Composition of the Co–Cr–Mo alloy: ASTM F-75, ASTM F-799 and ASTM F-1537 exhibits maximum

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Table 1
C, N, O content of raw elements

	C (ppm)	N (ppm)	O (ppm)
Co	50–200	<100	300–500
Cr	560–400	300–600	5000–7000
Mo	<100	<100	<100

nitrogen content only at 50, 500 and 2500 ppm, respectively.

(b) An HPPM (high pressure plasma melting) furnace was used to melt the alloys with a controlled nitrogen atmosphere. A DC power supply of 90 V was used.

(c) *Raw metal*: Industrial, pure grade metals Co, Cr, Mo with a purity of round 99.8% were used. Table 1 lists C, N and O contents. Table 2 specifies the melting atmosphere used in this study.

(d) The HPPM was first used with high-pure nitrogen gas (99.999%); then different pressures were employed to yield a different nitrogen level in the various alloys.

(e) *Composition analysis*: The compositions of the major alloy elements (Co, Cr, Mo) were measured with EPMA, while ICP-MS (inductively coupled plasma-mass spectrometer) was applied to determine the trace elements. The contents of C, O, N were determined by the Leco fusion technique.

(f) *Gleeble testing*: Samples were machined with electro wire cutting to L (15 mm) × D (10 mm), and then were heated to different temperatures (900, 1000, 1100, 1200, 1300 °C) to determine the optimum forging temperature.

(g) *Forging*: The melting ingots were then subjected to forging, with a forging ratio of 25%.

(h) *Heat treatment*: Homogenization was performed in a resistance furnace at 1100 °C for 4 h; the solution treatment was conducted in a resistance furnace at 1220 °C for 2 h; the samples were quenched in water [5], and then heated to 740 °C for 4, 6 and 8 h.

(i) *Tensile testing*: Tensile testing was performed at 10 kN on an MTS 810 system using standard ASTM-E8M sub-sized test specimens with a gauge length of 25 m. The mechanical properties of alloys were evaluated.

(j) *Roughness testing*: The polished samples were measured by a roughness tester (Surfcorder SE-2300). The value of R_a was graphed through a strip chart.

(k) *Wear testing*: Wear tests were performed on a multipurpose friction and wear tester (plint T53).

Fig. 1. Ingot in this study.

(l) *XRD analysis*: X-ray diffraction peaks were obtained from an X-ray diffractometer using monochromatic Cu Kα radiation at 600 W, 3 kV, and 20 mA. The intensity ratio was 0.5 and the 2θ scan range was set between 40° and 100°.

(m) *Optical microscopy*: The optical microstructure of specimens was elucidated by standard metallographical techniques. Samples were grounded with various coarsenesses of sandpaper and then polished with diamond paste down to 1 μm. Samples were finally electrolytically etched using the etchant of CrO_3 solution.

The grain size of the samples was determined using photo shop and scion image software.

3. Results and discussions

3.1. The ingot of HPPM

Fig. 1 shows the ingot melted with HPPM.

3.2. Nitrogen content in HPPM melted ingots

Table 3 presents the compositions of HPPM melted Co–Cr–Mo alloys. Nitrogen content increases with the pressure of the nitrogen atmosphere.

Table 2
HPPM atmosphere employed in this study

	HPPMC0N0	HPPMC0N1	HPPMC0N2	HPPMC0N3
Casting atmospheres (kg/cm^2)	1	2	3	4

Table 3
The compositions of Co–Cr–Mo in this study

Element (wt.%)	HPPMC0N0	HPPMC0N1	HPPMC0N2	HPPMC0N3
Cr	29.5	29.3	29.1	29.2
Mo	6.00	6.02	5.86	6.05
Ni	0.188	0.122	0.108	0.152
Fe	0.112	0.109	0.088	0.101
C	0.027	0.033	0.045	0.016
Si	0.049	0.073	0.038	0.039
Mn	0.041	0.034	0.073	0.051
O	0.015	0.013	0.022	0.044
N	0.014	0.096	0.189	0.288
Co	Balance	Balance	Balance	Balance

3.3. Surface roughness

Table 4 summarizes surface roughness data for HPPM Co–Cr–Mo alloys that underwent heat treatment. No big differences in roughness were observed among samples subjected to the same polishing process. The greatest roughness was observed in commercial sample (ASTM F-75 brand A) with a high carbon content of 0.36 wt.%.

Experimental results suggest that rougher Co–Cr–Mo wrought alloys possess a higher carbon content detrimentally affecting the performance of bone implants.

3.4. Effect of nitrogen contents on tensile properties

Except for the nitrogen content, the compositions of the ingots were within the specification of standard ASTM F-1537 wrought Co–Cr–Mo alloys.

The ingots reached the highest nitrogen content of 2880 ppm in HPPM melting, when the nitrogen atmosphere was set at 4 atm.

The tensile properties measured here, are described below. Figs. 2–4 present the effect of nitrogen content on tensile properties: elongation, yield strength, and UTS increase with nitrogen content.

The highest tensile strength, yield strength and elongation were observed in the HPPM melted ingot with a nitrogen content of 2880 ppm (C0N3).

The elongation of this alloy can be achieved up to 26.1%.

Table 4
Roughness, R_a (μm), of alloys under different heat treatments

	As-cast	As-forged	H4	A4	A6	A8
HPPMC0N0	0.08	0.09	0.10	0.09	0.04	0.08
HPPMC0N1	0.04	0.08	0.09	0.05	0.07	0.06
HPPMC0N2	0.06	0.05	0.06	0.09	0.04	0.06
HPPMC0N3	0.07	0.09	0.08	0.05	0.06	0.07
ASTM F-75 brand A	0.22	0.20	0.18	0.17	0.16	0.17

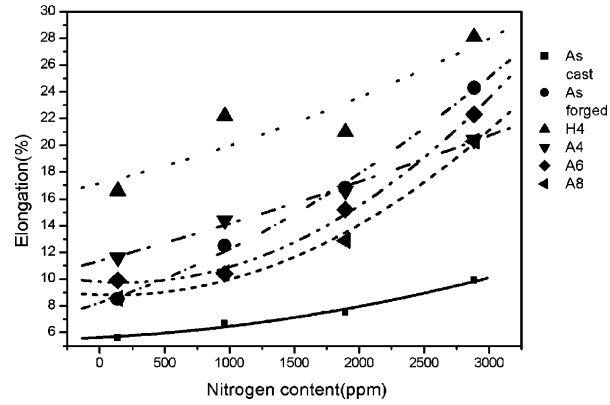

Fig. 2. The effect of nitrogen content on elongation.

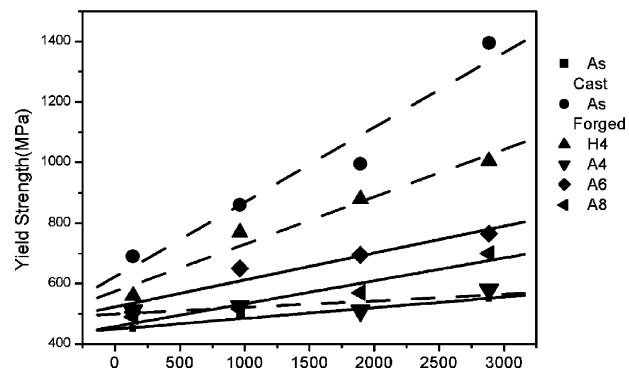

Fig. 3. The effect of nitrogen content on yield strength (YS).

3.5. Effect of nitrogen contents on wear properties

Wear data was obtained from the volume loss of samples subjected to sliding against a roller of the same composition, with a hardness of HRC 38 at a fixed distance of 8.9 km. Fig. 5 reveals that the lowest wear rate is found in samples with the highest nitrogen content (2880 ppm).

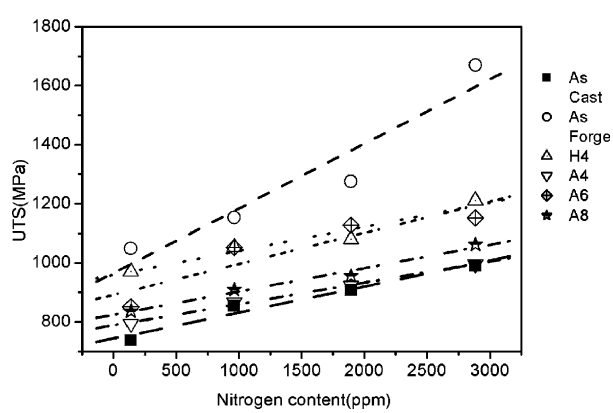

Fig. 4. The effect of nitrogen content on strength (UTS).

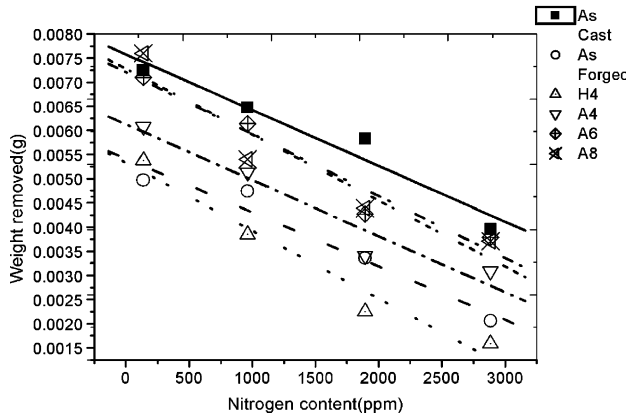

Fig. 5. Effect of nitrogen content on wear property.

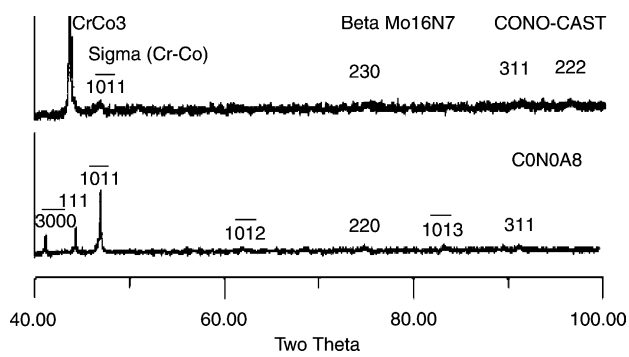

Fig. 6. The diffraction peaks on Co–Cr–Mo alloys.

3.6. The effect of HCP/FCC ratio

The X-ray diffraction of samples reveals no significantly preferred orientation or additional phase in the HCP and FCC microstructures in the alloys. Fig. 6 presents the diffraction peaks. The relative amounts of HCP/FCC phases were calculated semi-quantitatively by the product of the peak intensity counts and the peak width. Fig. 7 plots the wear-removed volume against the HCP/FCC ratio. The wear rate increased with increasing HCP/FCC ratio in this study.

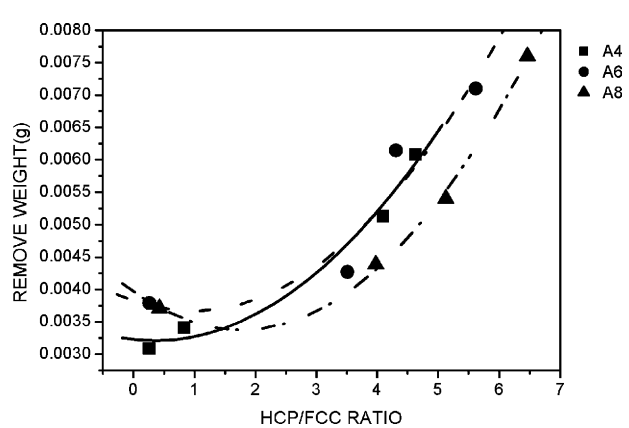

Fig. 7. The wear rate against HCP/FCC ratio.

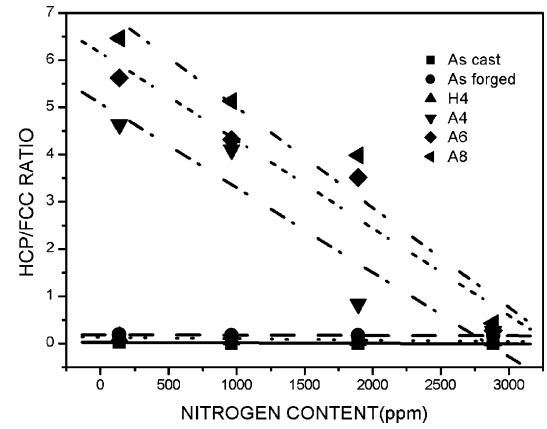

Fig. 8. The HCP/FCC ratio on different nitrogen content.

Table 5
The crystal grain size on different annealing treatments (μm)

	A4	A6	A8
HPPMC0N0	56	81	147
HPPMC0N1	50	82	136
HPPMC0N2	41	62	92
HPPMC0N3	37	43	59

Fig. 8 displays the variation of the HCP/FCC ratio with nitrogen content, revealing that FCC increases as the nitrogen contents increases.

A higher HCP/FCC ratio with an initially larger grain size induced by TRIP should not exhibit a higher wear rate [6].

3.7. The effect of grain size

Table 5 lists the grain size following solution aging heat treatment. Fig. 9 shows the relationship between the grain size and nitrogen content. The grain size varies modestly with heat treatment at high nitrogen content.

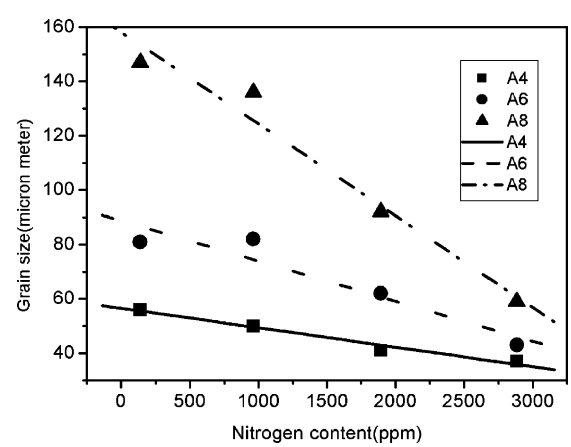

Fig. 9. The effect of nitrogen content on grain size.

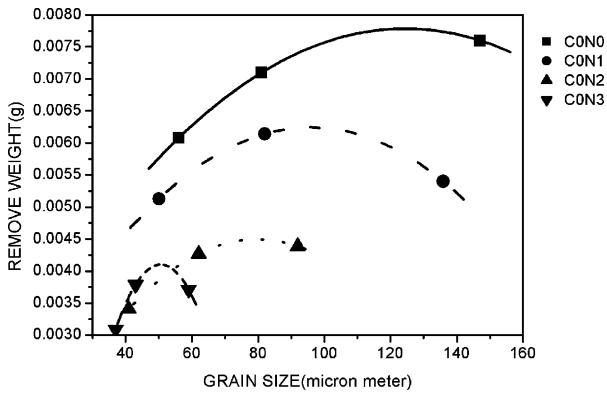

Fig. 10. Wear resistance against grain size.

Fig. 10 presents the relationship between wear rate and the grain size. Wear resistance varies with both nitrogen content and grain size.

4. Conclusions

1. Nitrogen can be feasibly added into Co–Cr–Mo alloys using HPPM, and 2883 ppm nitrogen could be achieved at a pressure of 4 atm.
2. HPPMC0N3 alloy with homogenization heat treatment promotes superior yield stress, elongation, and UTS.
3. The Co–Cr–Mo alloys with high nitrogen content showed better wear resistance properties, a finer grain size, and suitable ductility after undergoing homogenized heat treatment.
4. The primary factors that affect wear resistance in Co–Cr–Mo alloys are grain size and HCP/FCC ratio.
5. The results provided a material design for surgical implant alloys which will be used in metal-on-metal total knee replacement before biological testing.

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