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Microstructural characterization of low and high carbon CoCrMo alloy nanoparticles produced by mechanical milling

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Abstract. CoCrMo alloys are utilised as the main material in hip prostheses. The link between this type of hip prosthesis and chronic pain remains unclear. Studies suggest that wear debris generated in-vivo may be related to post-operative complications such as inflammation. These alloys can contain different amounts of carbon, which improves the mechanical properties of the alloy. However, the formation of carbides could become sites that initiate corrosion, releasing ions and/or particles into the human body. This study analysed the mechanical milling of alloys containing both high and low carbon levels in relevant biological media, as an alternative route to generate wear debris. The results show that low carbon alloys produce significantly more nanoparticles than high carbon alloys. During the milling process, strain induces an fcc to hcp phase transformation. Evidence for cobalt and molybdenum dissolution in the presence of serum was confirmed by ICP-MS and TEM EDX techniques.

1. Introduction

Hip replacement surgery is one of the most successful medical operations and has been a good treatment for arthritis and other joint diseases in terms of chronic pain[1]. Metal on metal (MoM) devices can provide longer lifetimes for these implants, and cobalt-chromium (CoCr) based alloys are increasingly utilized due to the characteristics of good longevity[2] and low wear[3], especially in the second generation of these implants.

Both high and low carbon CoCrMo alloys are utilised in MoM hip implants. The carbon plays an important role in the strength, ductility and wear resistance of the implants. Nevertheless, the carbon can induce the formation of carbides and these may become sites for localized corrosion (dissolution) [4]. As a consequence, ions and/or particles released in this process may interact with the surrounding tissue and lead to an inflammatory response.

This paper investigates ball milling of low and high carbon CoCrMo alloy gas atomized powders in order to simulate the effects of mechanical wear of the alloy during implant use. The characterization of the size, shape, composition and phase structure of these nanoparticles gives relevant information about the physicochemical behaviour in relevant biological media and any preferential dissolution of the elements. CoCrMo powders have been milled in bovine serum albumin achieving a particle size reduction to the nanometre scale. The nanoparticles generated are comparable in terms of size and composition to some of the nanoparticle wear debris produced by real hip implants[5].

The samples were analyzed by Transmission Electron Microscopy (TEM) (in terms of size and shape), Energy-Dispersive X-ray spectroscopy (EDX) (composition) and High-Resolution

Transmission Electron Microscopy (HRTEM) (phase identification). These results are compared to bulk techniques such as X-ray Diffraction (XRD), Dynamic Light Scattering (DLS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), demonstrating the effect of milling fluid on the size and stability of CoCrMo nanoparticles when in the presence of serum proteins.

2. Experimental techniques

CoCrMo gas atomized powders (ASTM75), both high and low carbon, were purchased from Sandvik Osprey. These starting powders had a particle size of around 22 μm and 16 μm, respectively. Bovine Serum Albumin (BSA), heat shock, pH 7.0 was acquired from Fisher Scientific, and used in solution during milling as a process control agent. The solution was composed of 0.4g of BSA diluted in 10 mL of deionized water. The powders were ball milled for 150 min in a high energy Spex 8000M mill using zirconia ceramic vial and balls. Before milling, the vial was fully filled with an inert gas (Argon) to avoid atmospheric contamination. A ball-to-powder weight ratio of 3:2 was used. After collection, samples were centrifuged in a Heraeus Megafuge for 10 min, at 25°C and a centrifugal force of 8000G. This procedure removes part of the BSA and coarse particles, maintaining most of the fine particles in dispersion.

Characterization by XRD was carried out using a Philips/PANalytical X'pert Diffractometer with Cu Kα radiation (λ = 1.5418 Å). The suspension was dropped onto a Si wafer and dried. TEM samples were analyzed using a Phillips CM200 FEGTEM operated at 200kV equipped with an Oxford Instruments UTW SDD EDX detector. Samples were drop cast onto lacey carbon coated Cu TEM grids. HRTEM images were acquired on an image-corrected FEI Titan 80-300 (S)TEM operated at 300 kV. For DLS, the samples were placed in an ultrasonic bath for 20 min. The refractive index and absorption coefficient used for hydrodynamic size analysis were 2.064 and 3.595, respectively.

3. Results and Discussion

3.1 Particle size and shape

The nature of the milling process could be comparable to the way that real wear debris particles are mechanically generated. The process includes the action of scratching and/or pounding of two CoCrMo surfaces, creating damage on the surface of the alloy. Shear bands are characteristic of this process and are often observed in particles – see Fig.2 (f).

The raw CoCrMo atomized powder shows perfectly round particle morphologies [Fig. 2 (g) and (h)]. After milling, DLS analysis [Fig.2 (a)] showed a significant decrease in particle size: a reduction down to 10-600nm for the high carbon and 10-800nm for the low carbon alloy powders. For both milled powders, the majority of the particles are found in the range of 10-200nm, and these results agree with TEM analysis in Fig. 1(b). By TEM, the low carbon alloy generated almost 50% more nanoparticles in the range of 10-200nm than the high carbon alloy. This could be related to carbon improving the ductility of the alloy, resulting in the absorption of more impact energy during milling.

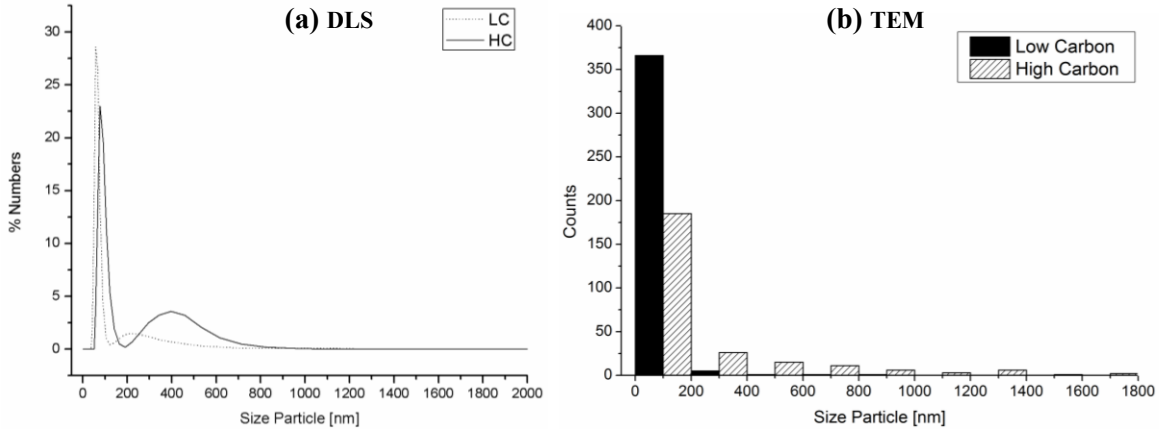

Figure 1 – (a) DLS and (b) TEM particle size distributions for the high and low carbon milled material.

3.2 Phase analysis

XRD of the raw material showed that both high [Fig.2 (a)] and low [Fig.2 (b)] carbon alloy powders, are dominated by the presence of the CoCrMo face-centred cubic phase (fcc, JCPDS 04-16-6869). Traces of the CoCr hexagonal close-packed phase (hcp, JCPDS 04-002-1030) are also evident. With the mechanical action of milling, post-milled material showed a significant increase in the hexagonal phase. This phase transformation is a strain induced fcc-hcp transformation (SIT), where temperature usually plays an important role, however in this case, stress is the most important contribution. The presence of carbon substantially alters the retention of the fcc phase after milling which is expected because carbon is known to stabilize this phase. S(TEM) analysis reveals coarse particles dominated by the fcc phase [Fig.2 (i)], whereas fine particles (less than 200nm) are predominantly hcp [Fig.2(e)]. This effect probably occurs due to the higher energy transferred to produce fine particles. In addition, XRD showed the appearance of zirconia traces (tetragonal, JCPDS 01-083-0113) as a result of contamination by erosion of balls/vial of the mill, possibly by hydrothermal degradation.

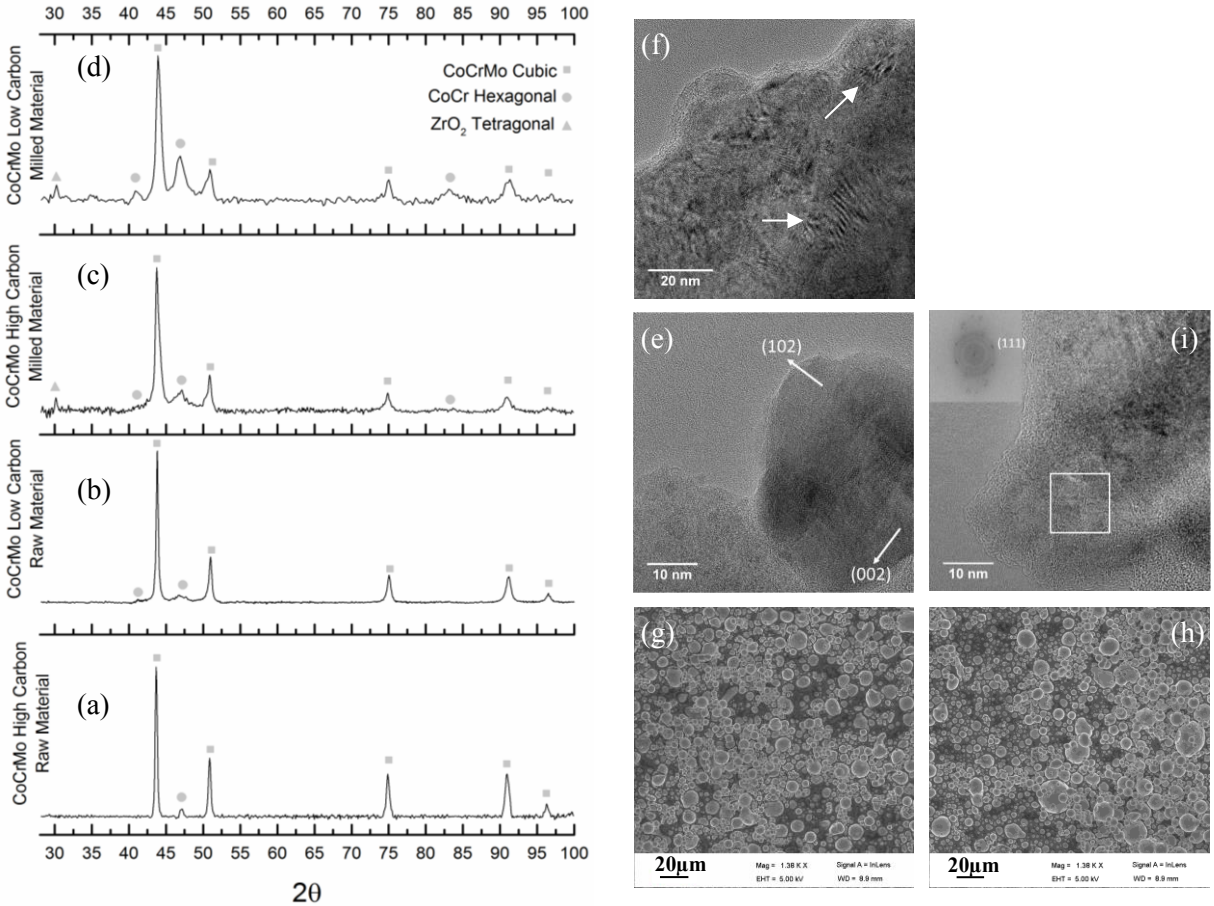

Figure 2 – Phase identification by XRD: (a) high carbon raw material, (b) low carbon raw material, (c) high carbon milled material and (d) low carbon milled material. TEM shows shear bands characteristic of milling process (f). TEM hcp and fcc phase identification in (e) and (i). SEM of the raw material: (g) low carbon and (h) high carbon powder.

3.3 Composition

The raw bulk materials were analysed in terms of composition (atom %) by SEM Energy Dispersive X-ray Spectroscopy (EDX). TEM-EDX [Fig.3 (b)] of individual particles showed that the low carbon milled material contained 75% of the particles with a cobalt composition below that of the raw material, accompanied by a corresponding increase in chromium. Following milling, high carbon alloy particles presented a wide distribution in composition. Some of the very small particles (about 10nm)

were composed of almost 100% cobalt. However, 50% of the high carbon particles were found with a cobalt composition below that of raw material. In both high and low carbon alloy powders, ca. 50% of the particles showed no presence of molybdenum (or a level below the detection limits of EDX), with the remaining 50% showing 10% to 20% Mo, above that found in the raw material. ICP-MS results [Fig.3 (a)] strongly suggest that cobalt and molybdenum undergo dissolution during the milling process in serum in agreement with the TEM results. This behaviour is apparently independent of the amount of carbon in the alloy. The difference in the absolute degree of dissolution between the high and low carbon powders shown in ICP is likely related to the Ostwald-Freundlich relation, where the particle solubility is inversely proportional to particle size, TEM having revealed that the low carbon alloy produced more nanoparticles. Moreover, ICP indicates that chromium is resistant to the dissolution process.

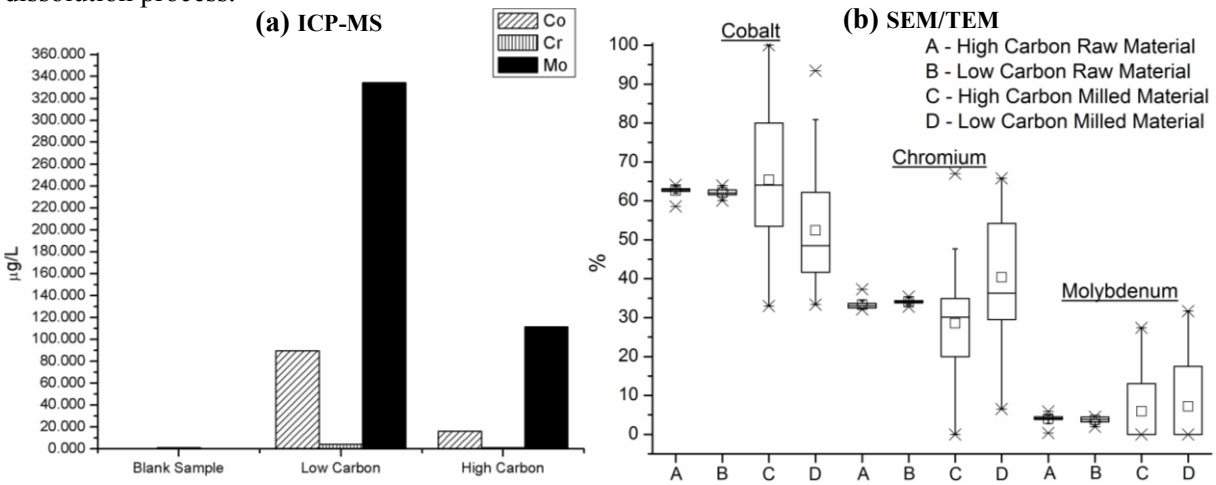

Figure 3 – (a) ICP-MS of low and high carbon milled material. (b) Boxplot† of TEM/SEM EDX of high and low carbon, raw and milled material.

4. Conclusions

Mechanical milling of CoCrMo-C alloy atomized powders has been shown to decrease particle size to between 10-200nm which is comparable with that seen in real wear debris released by hip implants. During milling, low carbon alloy powders generated more nanoparticles than the high carbon alloy, which is directly related to the mechanical properties and the stabilization of the fcc phase by carbon. ICP-MS together with SEM/TEM EDX gave an indication of cobalt and molybdenum dissolution in the presence of serum for both high and low carbon alloy milled powders. TEM shows a good agreement with bulk techniques, and allows differentiation of results in terms of particle size.

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† The bottom of each box is the 25th percentile; top is the 75th percentile; line in the middle is the medium value; square inside the boxes represents the average; "Whiskers" above and below each box represent 1.5 of the average values; crosses are the outliers.