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Research paper

New insights into hard phases of CoCrMo metal-on-metal hip replacements

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ABSTRACT

The microstructural and mechanical properties of the hard phases in CoCrMo prosthetic alloys in both cast and wrought conditions were examined using transmission electron microscopy and nanoindentation. Besides the known carbides of $M_{23}C_6$-type (M = Cr, Mo, Co) and M_6C-type which are formed by either eutectic solidification or precipitation, a new mixed-phase hard constituent has been found in the cast alloys, which is composed of ∼100 nm fine grains. The nanosized grains were identified to be mostly of $M_{23}C_6$ type using nano-beam precession electron diffraction, and the chemical composition varied from grain to grain being either Cr- or Co-rich. In contrast, the carbides within the wrought alloy having the same $M_{23}C_6$ structure were homogeneous, which can be attributed to the repeated heating and deformation steps. Nanoindentation measurements showed that the hardness of the hard phase mixture in the cast specimen was ∼15.7 GPa, while the $M_{23}C_6$ carbides in the wrought alloy were twice as hard (∼30.7 GPa). The origin of the nanostructured hard phase mixture was found to be related to slow cooling during casting. Mixed hard phases were produced at a cooling rate of 0.2 °C/s, whereas single phase carbides were formed at a cooling rate of 50 °C/s. This is consistent with sluggish kinetics and rationalizes different and partly conflicting microstructural results in the literature, and could be a source of variations in the performance of prosthetic devices in-vivo.

1. Introduction

During the past decade over 200,000 hip replacements have been implanted in the United States annually, and this number is expected to increase to 572,000 by 2030 (Kurtz et al., 2007). For conventional implants currently made of metal-on-polyethylene (MOP) bearings, the generation of polyethylene wear debris leads to osteolysis and has been shown to be a primary reason for early implant failure (Willert and Semlitsch, 1977). An alternative, CoCrMo metal-on-metal (MOM) implants complying with the ASTM F-75 standard, have been of extensive interest as an alternative to MOP bearings due to their excellent wear properties and corrosion resistance (Poggie et al., 1999). In addition, a beneficial tribological layer can be generated on the metal surfaces. Wimmer et al. reported that among 42 examined retrieved

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McKee–Farrar prostheses, 80% of them had tribological layers adhered firmly to the surfaces, which may act as solid lubricant (Wimmer et al., 2003) and is primarily graphitic carbon (Liao et al., 2011).

In addition to the Co, Cr and Mo, up to 0.35% weight percent carbon is incorporated in the alloys as carbides. These carbides significantly affect to the overall mechanical behavior of the CoCrMo alloy. It is generally agreed that fine carbide precipitates within the grains will increase the strength, while coarse ones at grain boundaries embrittle the material. Asgar and Peyton (1961) suggested that a spherical and discontinuous island carbide structure leads to the most ductility, and that carbides at grain boundaries reduce the ductility. While the overall mechanical properties are important, a CoCrMo implant is more than sufficiently strong to support the weight of a patient. The concern in a tribological system is more focused on how materials behave at the contacting surface. When two surfaces slide against each other, the load is carried by a number of asperities of nanometer to micrometer size. The wear medium, surface roughness and other extrinsic factors readily influence the friction. In a simplified model that only considers plastic deformation, the wear rate is inversely proportional to the hardness, i.e. the well-known Archard Equation (Hutchings, 1992). In a real tribological system, however, friction is much more complicated in that many other factors, including surface fracture, fatigue, grain rotation, and corrosion due to tribo-chemical reactions, can lead to loss of material. All these factors are related to the structure and chemical composition of the constituent phases and grain/phase boundaries, and their mechanical properties. For a hip replacement in service, the carbides usually serve as contact asperities in human synovial fluid due to their hard nature. Therefore the structural and mechanical properties of individual carbides directly affect the wear performance and should be carefully characterized. Wimmer et al. (2001) showed that carbides could be torn off under high local contact stresses, inducing surface fatigue by indentations and possibly lead to abrasion. The local contact stresses in such cases are dependent on the Young's modulus and hardness (Wimmer et al., 2001).

At room temperature, as-cast CoCrMo has an fcc metastable matrix due to its sluggish transformation to the stable hcp phase (Lopez and Saldivar-Garcia, 2008). Different kinds of carbides, e.g. $M_{23}C_6$, M_6C, have been reported in both cast and wrought alloys either at grain boundaries or in interdendritic regions. Asgar and Peyton (1961) examined as-cast CoCrMo and found carbides of different shapes, e.g. spherical discontinuous island-like carbides and continuous carbide films at grain boundaries. Clemow and Daniell (1979) solution treated an as-cast alloy at 1230 °C and found that interdendritic $M_{23}C_6$ carbides transformed to M_6C after 0.25 h annealing. Kilner et al. (1982) reported that the second phases of the lamellar structure in cast CoCrMo were predominantly $M_{23}C_6$ precipitates. After annealing at 1225 °C for 24–48 h, the $M_{23}C_6$ carbides dissolved into the matrix. The authors also observed long prismatic needle-like carbides which could possibly be M_7C_3.

The carbide structure, however, has not been fully analyzed due to the complexity of the CoCrMoC system. Conflicting results (Caudillo et al., 2002; Gomez et al., 1997; Taylor and Waterhouse, 1986) have been reported. For instance, Taylor and Waterhouse (1986) only observed a $M_{23}C_6$ blocky carbide after solution treatment at 1250 °C for 2 h using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Caudillo et al. (2002) solution-treated Co alloys but did not observe any other carbide structure apart from $M_{23}C_6$. In addition to the crystallographic structure, the reported chemical compositions of carbide precipitates are conflicting Clemow and Daniell (1979) reported that the fractions of Mo and Cr were 6% and 35%, respectively, while Devine and Wulff (1975) reported them to be 20% and 35%, respectively. The Mo content measured by Kilner et al. (1982) was similar to Devine and Wulff's results (Devine and Wulff, 1975), but the Cr content was 59%.

Clearly a more thorough understanding of the hard phases in the CoCrMo system is desired. In this paper, the carbides in both cast and wrought conditions are examined using electron diffraction techniques and the influence of different carbides on the wear performance is briefly discussed. We will also return, briefly, in the discussion to the issue of why different microstructures have been observed by different groups, suggesting that this is due to sluggish kinetics.

2. Experimental details

2.1. Materials

A number of different samples were analyzed. Initial work was done with a commercial high-carbon wrought alloy (ASTM F1537-94) and two retrieved MOM hip implant pairs (Depuy Orthopedics) of unknown state of heat treatment made of cast high-carbon CoCrMo alloy (ASTM F75-98). The two retrieved replacements served in patients for 604 days (age: 59 years) and 14.1 years (age: 90.7 years), respectively. The implant pairs were retrieved due to loosening of the acetabular component. Based in large part on the results obtained from these samples, the microstructure evolution of two additional samples were analyzed. In particular, the wrought alloy was re-melted in an argon atmosphere and cooled using two different treatments: (i) the melt was cooled in a water-chilled copper crucible to room temperature in ~30 s; and (ii) the melt was furnace cooled to room temperature in ~2 h. The cooling rates were ~50 °C/s for the former and ~0.2 °C/s for the latter.

2.2. Material characterization

The alloys were sectioned using a high-speed abrasive saw and mechanically polished using 0.3 μm alumina powder to a mirror finish. For general grain size analysis the surfaces were etched in a solution of 50 ml water + 50 ml HCl + 4 g $K_2S_2O_5$ for 30 s at room temperature. The surfaces were then examined with an optical microscope as well as a Hitachi S3400 scanning electron microscope (SEM) operated at 20 kV. The localized mechanical properties were examined using a Hysitron Tribo-indenter with a Berkovich-type diamond indenter at a maximum load of 4 mN. For these measurements the surface was scanned in atomic force microscopy (AFM) mode before and after the indentation.