Metal-On-Metal Total Hip Replacement Devices
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Microstructure of Retrievals Made from Standard Cast HC-CoCrMo Alloys

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ABSTRACT: During the past decade, self-mating metal bearings based on cobalt– chromium–molybdenum (CoCrMo) alloys have become very popular in total hip replacements and hip resurfacings. This led to a market share of more than 35 % for metal-on-metal (MoM) bearings in the United States before several cases of high wear with biologic consequences led to a sharp drop in popularity. In part, these failures are a result of a very shallow understanding of the wear mechanisms in MoM joints and their relation to the microstructure. In order to find such a relation, one has to keep in mind that the microstructures of metallic materials depend distinctly on the entire production sequence. In addition, they change markedly under tribological stresses. This paper does not discuss the wear of any specific retrieval or even try to relate that to the specific microstructure, because such a task would be impossible based on the unknown loading history of such retrievals. Thus, we depict only the possible range of microstructures from standardized high carbon (HC)-CoCrMo retrievals. These reveal different types of hard

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phases: carbides and/or intermetallic phases. Some are fine (<10 μm) and homogeneously distributed, whereas others appear as thin (<1 μm) and brittle cord-shaped arrangements at grain or dendrite boundaries. Coarser (>30 μm) types of mixed hard phases, which consist of carbides and intermetallic phases, often show microcracks already below the articulating surfaces. Such subsurface microcracks are known to destabilize the gradient below the surface and the balance between tribochemical reactions and surface fatigue. In this paper, the microstructures of retrievals manufactured from standard cast CoCrMo alloys are shown and evaluated.

KEYWORDS: cast, CoCrMo, metal-on-metal, MoM, microstructure, wear, carbides, intermetallic phases

Introduction

During the past decade, self-mating metal bearings based on cobalt–chromium–molybdenum (CoCrMo) alloys have become very popular in total hip replacements and hip resurfacings [1,2]. The latter emerged as an alternative for total hip replacements in young patients. This led to a market share of more than 35 % for metal-on-metal (MoM) bearings in the United States before several cases of high wear with biologic consequences lead to a sharp drop in their popularity [3–7]. Eighty percent of the failure cases cannot be explained by simple criteria such as high wear or high blood serum levels [8]. There is still a very shallow understanding of the acting wear mechanisms within the different contact areas of a hip joint and their effect on and contribution to the performance of the entire tribological system. It has been shown recently for ceramic joints that different mechanisms take place depending on the local loading situation [9]. Thus, on the basis of retrievals and their unknown specific loading history, it is impossible to find a close correlation between the wear behavior and the microstructure. One has to keep in mind in addition to the chemical composition, microstructures of metallic materials depend distinctly on the entire production sequence of casting, heat treatment, forging, machining, etc. In addition, even at small clinical wear rates of less than 2 μm/year, these incipient microstructures change markedly under tribological stresses into metallo-organic compounds consisting of wear particles of some tenths to hundredths of a nanometer in size and constituents of denatured proteins [10–17]. It has been shown recently in in vitro tests that under simulated hip joint loading conditions, the microstructure is sensitive to the loading conditions [18]. If the load is too small, the metallo-organic tribofilm is not generated at all, whereas at too-high loads it does not last and wear increases. In order to maintain this tribofilm, the desired combination of sliding wear mechanisms would be "tribochemical reactions" (TCRs) to generate the metallo-organic compound and "surface fatigue" (SF) to limit wear to it. Thus the surface and the subsurface microstructures must sufficiently support this [19,20]. Here the microstructure of the materials becomes another substantial element in the performance of hip joints, in addition to all the other manifold parameters influencing the clinical performance.

This paper does not try to relate the microstructure of retrievals to their wear behavior; because of the unknown loading history, this is not possible. This contribution presents only a selection of the wide range of different microstructures from standardized cast high carbon (HC)-CoCrMo retrievals and evaluates them in terms of their tribological behavior on the basis of the current but still low understanding of boundary lubricated sliding wear at very small wear rates.

Materials and Methods

Retrievals

The specimens for this paper were selected from a group of more than 40 cast MoM retrievals that had been analyzed during the past 12 years with regard to their microstructure and wear mechanisms. They were either selected from a former clinical study [21] or given to us after being retrieved from Rush University Medical Center (Chicago, IL). For this work, only those cast brands that showed a multiphase microstructure with different types of hard phases were selected; from these, six characteristic retrievals representing different microstructures were chosen as the basis for this contribution (Table 1). The exact processing parameters during casting, hot isostatic pressing, and further heat treatments have not been disclosed to the authors.

All samples were sectioned without the generation of any artifacts following an previously published protocol [13], which was further optimized in terms of the cutting sequence and the cleaning protocol [22].

Microscopy

The preparation of optical microscopy and scanning electron microscopy (SEM) samples required polishing and etching of the samples to visualize the

TABLE 1—*List of cast retrievals selected for this paper.*

Retrieval	Part		Months in Situ	Diameter, mm
1	Head	Cast, HIP	46	45
2	Head	Cast, HIP	41	51
3	Cup	Cast, HIP	20	46
4	Cup	Cast, HIP	n.a.	44
5	Head	Cast, HIP, SA	n.a.	44
6	Head	Cast	n.a.	46
7	Cup	Cast	61	58

Notes: HIP, hot isostatically pressed; SA, solution annealed; n.a., not available.

microstructure. Whenever edge sharpness in cross sections was essential, the samples were embedded into duroplast (Epovit, Bühler, Düsseldorf, Germany). Otherwise, the samples were glued onto a steel block using wax. Grinding and polishing were carried out by means of manual grinding and polishing processes. The samples were ground with 320 mesh size emery paper and then polished with 6 and 3 μm diamond paste on an ultra-pol cloth (Struers, WiIlich, Germany) and 1 μm paste on a micro-cloth (Struers, Willich, Germany). The etchant was a mixture of H_2O, 32 % HCl, and $K_2S_2O_5$.

For the SEM, a Hitachi S-3400 VP-SEM (Hitachi High-Technologies Canada, Toronto, ON, Canada) at Northwestern University (Evanston, IL) and a LEO 1530 Gemini (Zeiss, Wetzlar, Germany) at Universität Duisburg-Essen, Germany, were used in topography and atomic weight (Z) contrast modes. Both scanning electron microscopes were equipped with Energy Dispersive X-ray Spectroscopy (EDS).

Nanoindentation

Samples for nanoindentation measurements have to be flat and coplanar in order to prevent the tip from being damaged. Depending on the sample size, embedded and unembedded samples were used. To investigate the hardness of the hard phases, it was necessary in some cases to use polished samples because a surface roughened by the etching process makes it impossible to gain results. A micro-hardness tester (Duramin 5, Struers, Willich, Germany) was used to mark the locations of hard phases. The polishing protocol was the same as for the optical and secondary electron microscopy. The measurements were carried out using a Hysitron TI-950 TriboIndenter (Hysitron, Minneapolis, MN).

Transmission Electron Microscopy, EDS, and EELS Analyses

For the preparation of cross sections, different methods were utilized. As described in Ref 13, two corresponding segments of head and cup were glued onto each other's articulating surfaces by means of a suitable adhesive (Epoxy G2, Gatan, Munich, Germany); it was proved that this method does not lead to artifacts in this and other studies. The sample was fixed by a slotted pipe with a diameter of 2.5 mm and positioned in a brass tube of 3 mm diameter. The tube was cut into slices 400 μm in thickness. The cross section of one slice precisely exposed the segments of cups and head lying on each other separated by a small gap of hardened epoxide adhesive. Using grinding, dimple grinding (Model 656, Gatan, Munich, Germany), and ion milling (Pips691, Gatan, Munich, Germany), the sample was thinned to the desired thickness of about 40 nm. Afterward, the specimens were investigated using a Phillips EM 400 (Phillips, Eindhoven, The Netherlands). In order to observe chemical changes, a high resolution transmission electron microscope (TEM) (Tecnai F20, Phillips, Eindhoven, The Netherlands) with EDS and electron energy loss spectroscopy (EELS) was used as well.

For further high resolution EELS and energy filtered transmission electron microscopy analyses at Northwestern University, very thin samples were necessary. Therefore, a focused ion beam (FEI Helios NanoLab, Hillsboro, OR) was employed for accurate sample preparation. To protect the surface from damage caused by the electron and ion beam, the samples were sputtered with a 15 nm thick gold layer. After the desired location on the sample was found, a 300 nm thick platinum layer was deposited on the surface using the electron beam at 2 kV and 2.7 nA. After the sample was tilted about 52°, a second platinum layer with a thickness of 3 μm was put upon the first using the ion beam at 30 kV and 93 pA/0.28 nA. The surrounding bulk material was then removed with the Ga ion beam. To reduce ion-beam-induced artifacts, lower voltages and currents were used to thin the sample down to around 1.5 μm. Afterward it was loosened from the surrounding material using the so-called U-cut technique. By means of the Omniprobe, the sample could be lifted out and mounted on a TEM grid. The mounted sample was thinned using the ion beam with decreasing currents and voltages to minimize ion-beam-induced damage. Afterward the specimens were investigated using a TEM (JEM-2100F, JEOL, Tokyo, Japan) and a scanning TEM (HD2300A, Hitachi High-Technologies Canada, Toronto, Ontario, Canada).

Results and Discussion

In general, the multiphase microstructures of HC-CoCrMo alloys consist of a metal matrix with embedded hard phases (e.g., Cr-carbides). For toughness reasons, the volume fraction of hard phases and, therefore, the C-content of the metallic alloys is limited.

Microstructure

The metal matrix is a face-centered-cubic (fcc) CoCrMoC (γ-CoCrMo) solid solution of known low stacking fault energy [23,24]. This allows for distinct strain hardening via dislocations and twins and a strain-induced phase transformation from γ-CoCrMo into hexagonally close-packed ε-martensite under both monotonic and cyclic shear forces [14,15,20]. In a tribological contact, this leads to a distinct strain gradient from the bulk toward the surface characterized by such lattice defects in combination with a reduction of the effective grain size from some tens of micrometers to some tens of nanometers [13,22]. Whereas the base material may have a micro-hardness value of about 450 HV0.01, it increases toward the surface to 700 HV0.01 at about 1 μm below the worn surface [13].

Nanoindentation measurements of the bulk material revealed values of 6 to 7.3 GPa, and the Young's modulus ranged from 195 to 215 GPa, which is in the range reported by others [25].

The hardness of the bulk CoCrMo of retrievals scatters depending on the production route and sequence and results from the remains of cold and hot working and/or heat treatment. It is known that the processing parameters have a distinct influence on the microstructures and thus on the mechanical and chemical properties [26]. Because there is no precise information available from manufacturers about the exact production route, sequence, and parameters, we do not discuss them here.

Because of their strength and exceptional cold-working capacity, CoCrMo solid solutions should provide strong support for hard phases. Within this perspective it is important to notice that hard phases precipitate in different types, sizes, and distributions. In order to be able to sort this for tribological applications, we follow an earlier definition of the size and shape of hard phases for wear resistant Fe-, Ni-, and Co-based materials [27–30]. Those between 500 nm and about 10 μm are designated as "fine" hard phases, and those larger as "coarse" hard phases. From 100 to 500 nm, they are defined as "ultrafine," and anything below 100 nm is "nanosize."

It has been known for decades that CoCrMo alloys show different hard phases after casting and any further heat treatments [26]. One would expect Cr carbides of the $M_{23}C_6$ type (M = Cr, Co), but others like, for example, M_7C_3, as well as intermetallic phases (IPs) of Mo-, Co-, and Si-like (e.g., σ-type) phases, can be found [22,31] that have the same size as the eutectic carbides. The latter solidify from the melt as eutectic phases and therefore precipitate as fine lamellar hard phases (Fig. 1).

A solution heat treatment might partly bring these into solution, followed by reprecipitation and reshaping into more compact fine, ultrafine, and/or nanosize carbides. The nano-hardness values of fine $M_{23}C_6$ carbides range from 14 to 19 GPa. Even though M_7C_3 carbides have also been found, the majority are $M_{23}C_6$ with a Young's modulus of 250 GPa. The reprecipitation and/or reshaping process leads to different arrangements within the microstructure toward either a "cord-shape" arrangement (Fig. 2) of carbides, partly alternating with other fine hard phases, or a coarse hard phase consisting of a dispersion of ultrafine ones of different types (Fig. 3).

Obviously there are at least two different hard phases apparent according to the Z contrast: one with a higher and one with a lower atomic weight than the CoCrMo matrix. The latter are the known carbides of $M_{23}C_6$ type, which bond about 5.3 wt. % C [32]. The other phase must contain more heavier elements, which points toward the Mo-rich σ-phase.

The fine micrometer-size precipitates within the cord-shape arrangement hard phases could be determined as $M_{23}C_6$-type carbides by means of TEM, EDS, EELS, and CoMo-IPs (Fig. 4).

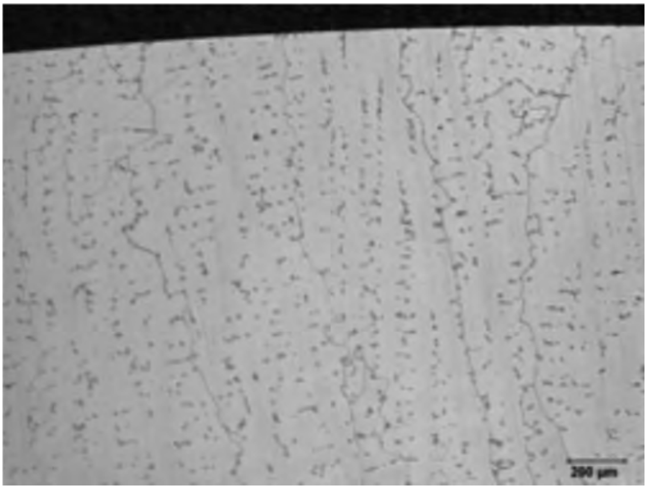

FIG. 1—*Typical microstructure of a cast high-carbon ASTM-F75 CoCrMo alloy in a cross section from retrieval 1.*

All constituents are separated by clear boundaries. The EDS elemental distribution maps of this area show that $M_{23}C_6$ bonds predominantly Cr together with a distinctly smaller amount of Mo and very little Co (Fig. 5, area 1). The IPs contain mostly Mo and Co and, obviously, are enriched with Si (Fig. 5, areas 2 and 3).

According to Gupta [33], six different IPs exist within the Co–Cr–Mo system, of which three contain mainly Co and Mo and three mostly Co and Cr. On the basis of the EDS and TEM diffraction analyses, it was found that the

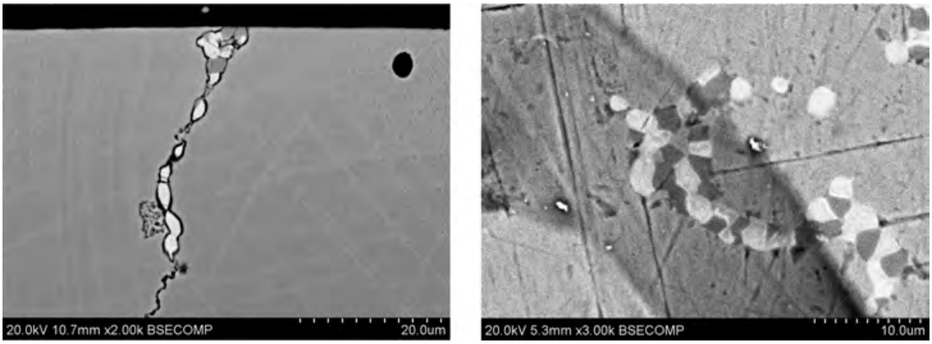

FIG. 2—*Cord-shape type arrangement of hard phases in a cross section (left) and at the worn surface (right) from retrieval 2. The Z-contrast (Z = atomic number of element) depicts two different hard phases, of which the lighter has a higher atomic weight and the darker a lower atomic weight than the metal matrix.*

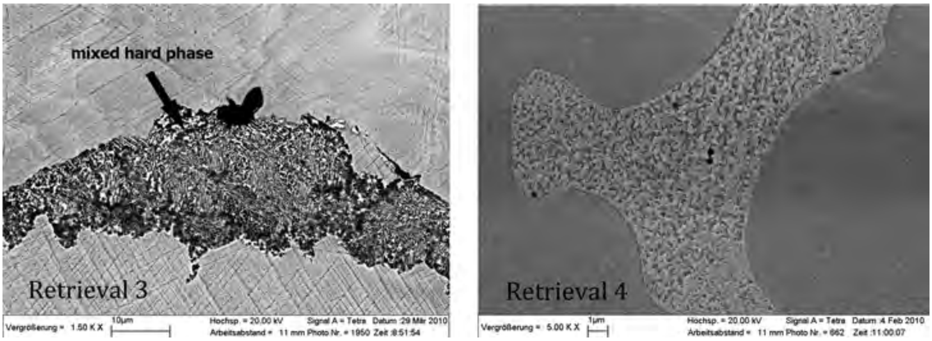

FIG. 3—*Lamellar and globular appearance of "mixed"-type hard phase in cross sections consisting of ultrafine and nanosize constituents.*

cord-shape arrangements consist of tetragonal Co_9Mo_{15} (σ-phase) and fcc $M_{23}C_6$ (τ-carbide).

The "mixed" hard phases consist of similar constituents like $M_{23}C_6$ and IPs, but because of the ultrafine and nanometer-size precipitates, the generation process must differ from that of the cord-shaped ones (Fig. 6).

Such mixed phases also show distinct grain boundaries between the ultrafine carbides and IPs. Interestingly enough, more than just one type of IP has been found in such constituents [22]. According to EDS and TEM diffraction analyses, there is an indication of a Co-rich and a Cr-rich σ-phase, but this is not yet fully verified and needs further analyses. Still, such mixed phases have been designated as carbides in the past [34]. Because of the shape of this mixture, both must have been precipitated simultaneously and appear as either

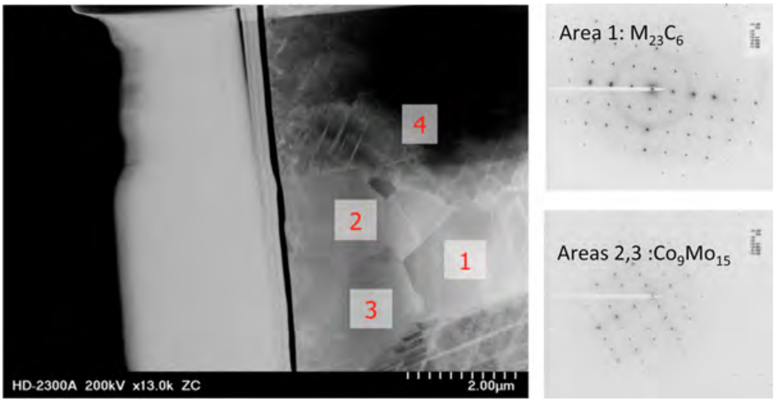

FIG. 4—*TEM-atomic number contrast image within cord-shaped hard phases of Fig. 2 over several carbide–IP boundaries and diffraction patterns. Area 4: fcc-CoCrMo solid solution.*

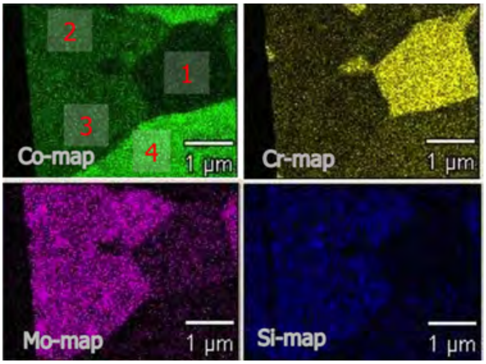

FIG. 5—*EDS elemental distribution of Fig. 4 of the main alloying elements Co, Cr, and Mo together with Si.*

globular or lamellar, depending on the orientation of the specimen taken. Because of the ultrafine to nanosize grains, it is most likely that they precipitate during a solid–solid "eutectoid-type" phase transformation [31]. The nanohardness of such mixed hard phases ranges from 8 to 11 GPa, and the Young's modulus is 200 GPa.

Evaluation of the Impact of Hard Phases on Sliding Wear

Today there is still very little understanding of the relationship between the microstructure and the wear of multiphase materials under boundary lubricated sliding wear at very small wear rates. This accounts for the fact that only a few nanometers of material (or less) are worn during one contact, whereas typical constituents are of micrometer size. Thus the so-called systems approach

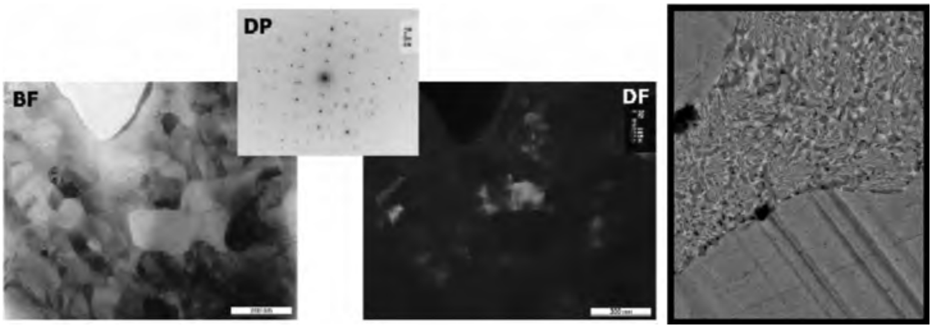

FIG. 6—*SEM Z-contrast (right) of a mixed hard phase within the primary articulating area of retrieval 7. TEM bright field (BF) and dark field (DF) images and diffraction pattern (DP) of a mixed hard phase. The atomic weight contrast shows different constituents, and the diffraction pattern depicts two overlapping lattices of $M_{23}C_6$ and an IP, which is still to be defined.*

should allow for a first attempt at evaluation. This approach was brought about in the late 1970 s by Czichos and Dowson [35] and successfully connected to the microstructure of metals, polymers, and ceramics by many authors later on for other types of wear, but at wear rates orders of magnitude larger. Zum Gahr compiled that research in 1987 [19]. The application of the systems approach to hip joints has been published previously by two of the current authors [36] and should not be repeated here in detail. In general, it describes the type of wear (here, sliding wear) being characterized by the structure and loading of the tribological system and the combination of acting wear mechanisms (here, TCR and SF). These two wear mechanisms are known to allow for small wear rates if TCR steadily generate a sufficient tribofilm being worn only by SF. The other two wear mechanisms, adhesion and abrasion, destroy or remove the tribofilm immediately. Adhesion would lead to high friction and finally seizure, whereas abrasion as the main wear mechanism brings about wear rates in the range of some micrometers per hour, instead of the known clinical wear rates of some micrometers per year. Still, grooves and scratches are always found on retrievals even at small wear rates, and therefore some abrasion must take place, but only occasionally [10,11]. Now the question is whether the IPs can act like carbides and improve the wear resistance against occasional abrasion. According to the known submechanisms of abrasion, this would require a certain hardness combined with sufficient toughness of the metallic alloy itself and all its constituents (hard phases, metal matrix, and phase boundaries) [19]. For the retrievals investigated here, the latter is questionable because, obviously, the fine IPs are not well supported by the matrix and tend to fracture. Figure 7 shows a cross section that has been prepared via a very smooth polishing process used for metallographic investigations.

Even under such low loads, some of the hard phases partly fell out of the cord-shape structure, whereas most of the carbides remained. Similar observations have been made in other retrievals with a cord-shape arrangement too. Others depict the brittleness of the IPs by showing microcracking of the IPs within the primary articulating area (Fig. 8). Also, for the mixed hard phases, the mechanical stability appears to be low, as they often show cracks directly underneath the contact surface (Fig. 9).

As mentioned earlier, it has already been shown and discussed by many authors that carbides and IPs precipitate from the melt or from solid solution and might transform into new phases based on the cooling rate or on further heat treatment of cast alloys [31]. In addition, wear tests have been run in order to investigate the influence of heat treatment on microstructure and wear behavior [34,37–39]. Unfortunately, many of these tests were run under predominantly mechanically dominated wear mechanisms (e.g., abrasion). For many applications of Co-base materials in mechanical or mining engineering, this is appropriate, because there abrasion is the main wear mechanism. Still, this does not represent those mechanisms acting in a well-functioning MoM

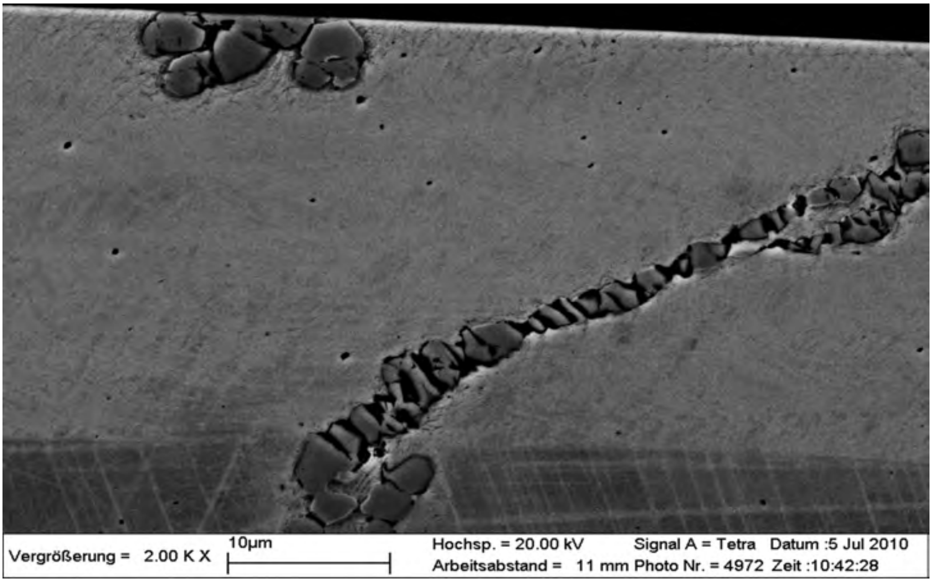

FIG. 7—*Pits and holes generated within a cord-shaped arrangement of hard phases of retrieval 5 (cross section).*

hip joint, which operates predominantly under tribochemical reactions and surface fatigue [10,11]. Thus, until today, no direct and unequivocal correlation between the microstructure and the wear of CoCrMo alloys under loading conditions characteristic of hip joints has been available. Existing hip simulator studies have revealed differences under different types of loading, but they

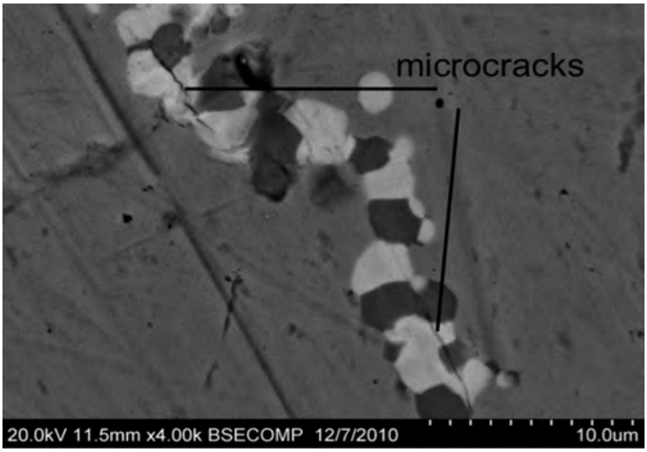

FIG. 8—*Microcracks within IPs (lighter phase) within the primary articulating area of retrieval 2.*

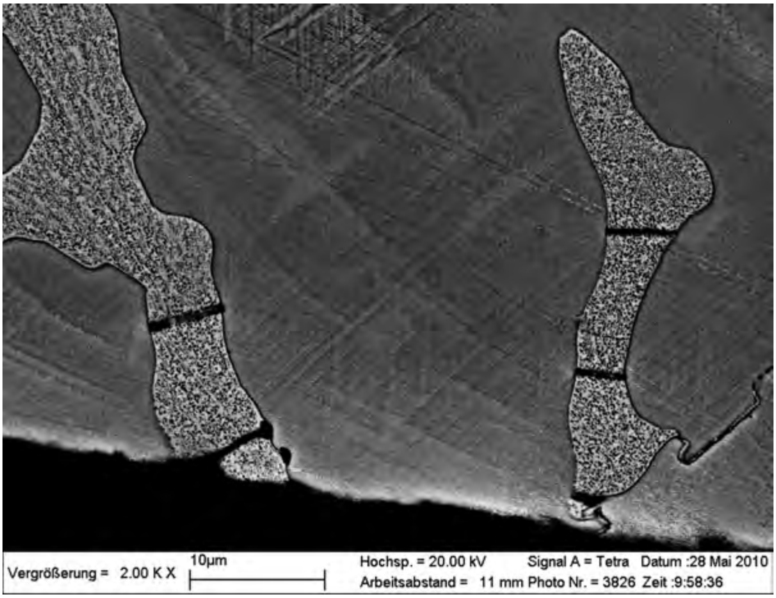

FIG. 9—*Cracks within the mixed hard phase underneath the primary articulating areas of retrieval 6 (cross section).*

have not been brought into relation with the acting mechanisms or the microstructure.

From more than five decades of microstructure-related wear investigations, it is known that under sliding wear of metallic surfaces, the role of hard phases is disputable [19]. Their role strongly depends on size, shape, distribution, interfaces to the matrix, etc. Concerning hip joints, certainly the picture slightly suggests a benefit of hard phases, but they could either improve the wear behavior or have no measurable effect at all [40,41]. Nevertheless, a hip joint implanted into a human body might require hard phases so that any hard particles being introduced into the articulating surfaces from outside like, for example, bone cement will not destroy the entire tribosystem immediately. Thus one might need hard phases for the “robustness” of such an implant. If so, they should help protect against occasional abrasion and therefore fulfill the criteria for metal-based materials with hard phases [42,43]. Taking this into account, it appears questionable whether the presented microstructures from the retrievals in Figs. 2 and 3 might fulfill such criteria at all.

Carbides like $M_{23}C_6$ solidify as fine, lamellar precipitates at dendrites or grain boundaries from the melt. With a maximum content of 0.35 wt. % C, the volume fraction of $M_{23}C_6$ is limited to about 7 vol. %, and their size and distribution can be controlled by the solidification rate. Otherwise, forging might be necessary; at a high enough forging ratio, the grain size decreases and the solution and reprecipitation/reshaping of carbides lead to an even distribution of fine hard phases. For a given amount of hard phases, this is the optimal microstructure for defending against abrasion, as has been shown for ledeburitic cold-work tool steels of D2 type, provided that the hard phases are supported sufficiently by the matrix [44].

The fine IPs within the microstructures of the investigated retrievals do not fulfill such criteria. Apparently these are brittle constituents and tend to generate microcracks. In addition, they seem to have no sufficient bonding to the matrix, which gives rise to their being torn off the surfaces and acting as micrometer-size wear particles themselves. This must lead to either two- or three-body abrasion with microploughing and microcutting as submechanisms [19]. If such brittle particles are introduced into the contact, they will further bring about microcracking, another submechanism of abrasion, which is accompanied by a further increase in the wear rate. Apparently there is a detrimental influence on the mechanical properties of the “fine” IPs as well, as already reported in Ref 31.

The “mixed” hard phase with ultrafine or nanometer-size IPs might not increase wear per se, because such small fragments will mainly roll over the surface and do not allow for a distinct amount of surface fatigue. The marked disadvantage of these constituents arises from the fact that they generate cracks already below the surface. Thus some material might fracture from it and be torn off the surfaces as micrometer-size particles. In parallel, the subsurface cracks destabilize the strain gradient by introducing sharp voids. In addition, the size of the ultrafine IPs puts them into the critical range of particles triggering adverse biological reactions [45].

Conclusions

Different early failure cast MoM retrievals were analyzed with regard to their microstructure.

- All retrievals showed a multiphase microstructure consisting of a CoCrMo metal matrix with embedded fine and coarse hard phases.
- According to their appearance, they were designated as either cord-shaped arrangements of carbides and IPs or “mixed” hard phases, both precipitating at grain boundaries.
- The cord-shaped arrangement consists of an alteration of compact fine Cr carbides and CoMo σ-phase intermetallics, whereas the mixed phase consists of lamellar or globular Cr carbides and, presumably, CrCo σ-phase.
- According to nanoindentation measurements, all hard phases are harder than the metal matrix, whereas the IPs show very brittle behavior.
- The latter might give rise to microcracking, a submechanism of abrasion that is known to increase wear.
- Further studies are needed as to the relation between the microstructure and the wear behavior of HC-CoCrMo alloys under mechanisms that are characteristic of hip joints.

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