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The Tribological Difference between Biomedical Steels and CoCrMo-Alloys

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Abstract

In orthopedic surgery different self-mating metal couples are used for sliding wear applications. Despite the fact that in mechanical engineering self-mating austenitic alloys often lead to adhesion and seizure in biomedical engineering the different grades of Co-base alloys show good clinical results e.g. as hip joints. The reason stems from the fact that they generate a so-called tribomaterial during articulation, which consists of a mixture of nanometer small metallic grains and organic substances from the interfacial medium, which act as boundary lubricant. Even though stainless steels also generate such a tribomaterial they were ruled out from the beginning already in the 1950 as “inappropriate”. On the basis of materials with a clinical track record this contribution shows that the cyclic creep characteristics within the shear zone underneath the tribomaterial are another important criterion for a sufficient wear behavior. By means of sliding wear and torsional fatigue tests followed by electron microscopy it is shown, that austenitic materials generate wear particles of either nano- or of microsize. The latter are produced by crack initiation and propagation within the shear fatigue zone which is related to the formation of subsurface dislocation cells and, therefore, by the fact that a Ni-containing CrNiMo solid solution allows for wavy-slip. In contrast to this a Ni-free CrMnMo solid solution with further additions of C and N only shows planar slip. This leads to the formation of nanosize wear particles and distinctly improves the wear behavior. Still the latter does not fully achieve that of CoCrMo, which also shows solely planar-slip behavior. This explains why for metallurgical reasons the Ni-containing 316L-type of steels had to fail in such boundary lubricated sliding wear tribosystems.

1. Introduction

In orthopedic surgery several self-mating metal couples are used for different applications such as screws, bone plates (Vadiraj and Kamaraj, 2006; Weinstein et al., 1973), total disc and hip arthroplasty (THA) (Bono and Garfin, 2004; Jacobs et al., 1994; Scales and Lowe, 1972; Stanton and Eck, 2010; Valdevit and Errico, 2004) as well as surface replacements (SR). For the hip, stainless steel couples were already tested 70 years ago by Wiles (Wiles, 1949; Wiles, 1958) and the Judet brothers (Sherk, 2003), however, these bearings failed for various reasons. As reported by Wiles (Wiles, 1958), McKee (McKee and Watson-Farrar, 1966) and Scales (Scales, 1956), stainless steel appeared “inappropriate” for self-mating

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bearing couples in THA. In addition, titanium was also tested and ruled out from the beginning (Scales, 1956; Scales, 1965). Thus, McKee and Farrar chose self-mating CoCrMo alloys (McKee and Watson-Farrar, 1966) as their bearing of choice based on the work with the Stanmore hip, as reported by (Duff-Barclay et al., 1966).

During the past decade self mating metal bearings based on cobalt-chromium-molybdenum (CoCrMo) alloys became very popular in THA and SR. Metallic materials allow more design freedom than their ceramic and polymeric counterparts. For example, hip resurfacing emerged due to the availability of self-mating metal joints and provided an alternative for total hip replacement in young patients. This led to a market share of up to 40 % (Kurtz et al., 2011) for metal-on-metal (MoM) bearings in the United States before several cases of catastrophic wear with terrible biologic consequences lead to a sharp drop in popularity (Mahendra et al., 2009). In part, these failures are a result of a very shallow understanding of the wear mechanisms in MoM joints as well as their relation to the microstructure. In order to be able to find such relation one has to keep in mind that microstructures of metallic materials change distinctly under tribological stresses. Thus one needs an incipient structure which is able to transform into the one, which provides appropriate tribological properties.

2. Background and Study Design

Sliding wear of metals can be characterized in general by the relative movement of two sliding surfaces and the contact load. Under those conditions, the surfaces continuously alter their topography, chemistry as well as the near surface microstructures (Zum Gahr, 1987). All four major wear mechanisms (Adhesion, Abrasion, Surface Fatigue, Tribochemical Reactions) can take place by itself or in combination. For an artificial hip joint sliding wear is characterized by a complex multidirectional motion under boundary or mixed lubrication (Hall and Unsworth, 1997; Hall et al., 1994; Paul et al., 2003; Saikko and Caloni, 2002; Scholes et al., 2000). This allows for wear rates ranging over more than ten orders of magnitude. Typically, self-mating face-centered-cubic (fcc) metal couples are not the best choice, because adhesion might become dominant and increase the wear distinctly or even lead to seizure (Buckley, 1984; Buckley, 1977; Sikorski, 1964). This led to the generally applied engineering principle that fcc metals should not be self-mated in the case of dry or boundary lubricated wear.

There are some self-mating fcc couples that do not adhere to this rule and allow for ultra-mild sliding wear. In such materials a so-called tribomaterial is generated during articulation consisting of a mixture of nanometer small metallic grains and substances from the interfacial medium, which then can act as boundary lubricant (Dienwiebel and Pöhlmann, 2007; Rainforth et al., 2002; Rigney and Glaeser, 1978; Rigney and Hammerberg, 1999). This nanostructured tribomaterial will allow for the high shear rates between the contacting bodies. For the hip joint, the average relative velocity difference between head and cup during walking is in the range of 0.13 m/s. With a tribomaterial thickness in the range of 150 nm (Büscher and Fischer, 2003; Büscher et al., 2005a; Pourzal et al., 2009a; Pourzal et al., 2009b; Wimmer et al., 2003) as it has been found experimentally, the shear rate would be about 0.8×10^6 1/s. In order to sustain such shear rates, the proteins of the neo-synovial fluid must either adhere strongly to the surfaces (Benz et al., 2004; Heuberger et al., 2005) by a still unknown mechanism (Yan et al., 2006a; Yan et al., 2006b) or be incorporated into the 100 to 400 nm thick tribomaterial generated by a submechanism of tribochemical reactions called “mechanical mixing” (Rigney and Hammerberg, 1999; Wimmer et al., 2009).

Even though the contact stresses of 50 MPa in the primary articulating area appear small compared to the mechanical properties of such fcc materials (Bergmann et al., 2001; Bergmann et al., 2004; Fischer, 2009; Yoshida et al., 2006) it is not fully clear while a 316L

stainless steel should not work in such contact situation. Büscher et al. showed in 2005 that 316L exhibited a 10 times larger wear rate than low carbon-CoCrMo (Büscher, 2005). In addition, it was pointed out that this larger wear rate is accompanied by 1000× larger wear particles (Figure 1)(Büscher, 2005). Certainly, such big particles would decrease the real contact area distinctly compared with the nanometer size wear particles of CoCrMo (Figure 1b), which act as solid lubricant. Size-by-size comparisons of wear particles and thickness of tribomaterial suggest that the nanosize wear particles of low wearing materials such as CoCrMo detach from the tribomaterial (Figure 2) (Büscher, 2005; Pourzal et al., 2009a; Wimmer et al., 2009). In contrast, the 10 to 50 µm large wear particles of the 316L-steel must have detached further below within the so-called shear zone (Figure 2). This is, because underneath the tribomaterial a strain gradient is formed by friction induced cyclic shear stresses (Dautzenberg and Zaat, 1973a; Dautzenberg and Zaat, 1973b; Rigney, 1998).

Using materials with a clinical track record, we will show that cyclic creep (ratcheting) is responsible for the microstructural changes observed on retrieved and laboratory tested materials. We will also show that these (dynamic) changes of the microstructure will determine the tribological properties of such self-mating applications and govern, whether it will be severe, mild or ultra-mild sliding wear*. Thus, in addition to wear tests, torsional fatigue tests have been carried out to mimic the cyclic shear stresses of frictional forces below the interfaces of such bearing and answer the question why self-mating stainless steel couples generate large wear particles and fail in sliding wear tribosystems while CoCrMo generates nanosize particles and does not fail.

2. Materials and Methods

2.2 Materials

For this investigation solution annealed face-centered-cubic (fcc) alloys for biomedical applications have been chosen X5CrNiMo17-13-2 (1.4441, AISI 316L), the low-carbon Co-base alloy CoCr29Mo6 (DIN ISO 5832-6) and two so-called high-Nitrogen-steels X6CrNiMnMoN22-10-4-3 (REX734, DIN ISO 5832-9) with 0.04 w-% C and 0.4 w-% N and the Ni-free X13CrMnMoN18-14-3 (1.4452) with 0.07 w-% C and 0.8 w-% N. All materials exhibited a fcc lattice structure with some remaining twins and/or stacking faults prior to testing (Figure 3). Except for the CrMnMoN steel with an average grain size of 103 µm the other materials exhibited a mean value of about 30 µm.

2.3 Dry Sliding Wear Tests

The dry sliding wear tests were carried out on a disc-on-pin tribometer (Wazau, Berlin, Germany) under the parameters given in table 2 and reported elsewhere by (Büscher, 2005; Büscher et al., 2005b). The frictional moment was measured at the rotating disc and transformed into the frictional force acting at the middle of the wear track at a radius of 9 mm. The weight changes ΔG of discs and pin were measured after 10, 20 50, 100, 200, 50050,000 and 90,000 rotations, respectively, (AC211s, Sartorius, Göttingen, Germany) following a thorough ultrasound cleaning in Acetone and the dimensionless wear rate W of the system was derived by those of disc and pin derived separately and added afterwards as follows with the density of the materials ρ , the length of the wear path L and the nominal contact area A , which could be measured directly at the worn surfaces of the

*The term ultra-mild sliding wear refers to wear rates of 1 to 10 nm/h. Such wear rates typically infer that less than one atomic layer is removed per sliding stroke. It shall distinguish from mild sliding wear, which is also characterized by a predominantly elastic interaction of the triboelements, but at wear rates in the range of 1 µm/h. Neither term nor magnitude are standardized and have been chosen facultatively.

specimens. In order to avoid new run-in phases the pins were remounted after each measurement exactly in that direction as they have been dismantled from.

2.4 Torsional Fatigue Test

The torsional fatigue tests were carried out by means of stress controlled incremental step tests at 1 and 25 Hz (MTS Bionix, MTS, Berlin, Germany). The special watch-glass shape of the fatigue specimens are published elsewhere (Tikhovski et al., 2002). The shear stresses were raised by 25 MPa every 5000 cycles up to a maximum of 700 MPa at an R-value of 0.1. Thus every test runs for about 90,000 cycles. Simultaneously the shear strains were measured in order to gain stress-strain hystereses of every 30th cycle. From these the shear stresses and shear strains, especially the mean plastic shear strain, were derived according to standard methods (Christ, 1991). The measured torsional or shear angle γ was then transformed into the equivalent strain ϕ_v by as described in (Dautzenberg and Zaat, 1973a). After testing the fatigue specimens were cut in the middle of the measuring length and samples were taken directly at the surface for metallographic inspection by means of transmission electron microscopy (TEM). The preparation techniques for surface samples was similar to that of the worn surfaces and was carried out as described in the following chapter.

2.5 Light and Scanning Electron Microscopy and Sample Preparation

All metallographic samples or cross sections from worn or fatigued specimens are sectioned at each preparation step by wet cutting devices of different sizes and brands avoiding any thermal heating. Light microscopy (LM) was carried out by means of a Metallux 2 Microscope (Leitz, Wetzlar, Germany) up to 500times magnification. The samples were ground with SiC-paper from 320 to 100 mesh size and afterwards polished with diamond suspension with grains sizes from 6 to 1 μm (ATM, Altenkirchen, Germany). Etching was done in V2A-etchant (100 ml aqua dest., 100 ml nitric acid, 5 droplets of pickling inhibitor) at 65°C for up to 50 s.

Scanning electron microscopy was done on worn surfaces by means of a HR-FE-SEM (LEO 1530 Gemini, Zeiss, Wetzlar, Germany) with attached energydispersive X-ray spectroscopy (EDS).

2.6 Transmission Electron Microscopy and Sample Preparation

For the preparation of cross sections the method developed by Büscher et al. has been used (Büscher et al., 2005a) and proved to be free of artifacts in this and other applications as well (Hahn et al., 2009; Runiewicz et al., 2006; Shakhvorostov et al., 2007). Here, two corresponding segments of head and cup were taken and glued onto each other's articulating surface by means of a suitable adhesive (Epoxy G1, Gatan, Munich, Germany). 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 to slices of 400 μm 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. Afterwards the specimens were investigated by means of transmission electron microscopy (EM 400 Phillips, Eindhoven, Netherlands). In order to observe chemical changes in the uppermost surface layers, a high resolution TEM (Tecnai F20 Phillips, Eindhoven, Netherlands) with EDS and electron energy loss spectroscopy (EELS) was used (Pourzal et al., 2009b).

3. Results

3.1 Tribological Behavior

3.1.1 Wear Rate—Figure 4 depicts the dimensionless combined wear rate of pins and discs of the tested couples showing a distinct run-in behavior. During this run-in some of the specimens gained weight in the very beginning, which can be attributed either to material transfer from pin to disc and vice versa or to tribochemical reactions. These results are not shown. After about 20 m all specimens lost weight with increasing test duration.

The wear rates of the CrNiMo- and the CrNiMnMoN-steels are nearly the same over the entire test period. According to the measured values the run-in period ends after about 2 km. It should be noticed here that the double-logarithmic diagram does not show this as distinct as a linear one would. But for the comparability of all wear rates over 10 orders of magnitude the double logarithmic style has been chosen. The steady state wear rate is 8.5 and 7×10^{-8} for the CrNiMo and the CrNiMnMoN-steel, respectively, which in other terms would be 25 or 30 $\mu\text{m/h}$. Thus, these wear rates are in the mild-sliding wear regime. Under steady state conditions the coefficient of friction scattered at a mean value of 0.45 ± 0.25 for CrNiMo and 0.35 ± 0.14 for CrNiMnMoN, while during run-in both were not distinctly different.

The CrMnMoN-steel and the CoCrMo-alloy reveal much smaller wear rates after 2 km. It is not clear whether even after 20 km steady state was reached, but the tests were stopped at this point, because the differences in weight were so small that the resolution of the scale of 0.1 mg was reached. This brought about wear rates of 2×10^{-9} for the CrMnMoN steel and 2×10^{-10} for the CoCrMo alloy. The latter would equal to about 100 nm/h, which is still one order of magnitude higher than ultra-mild sliding wear. Again the friction torque scattered resulting in an average coefficient of 0.54 ± 0.26 for CoCrMnN and 0.45 ± 0.22 for CoCrMo, respectively, and did not change over the entire test period.

3.1.2 Wear Appearances—Wear appearances for the CrNiMo- and CrNiMnMoN-steel with the higher steady-state wear rate are quite similar showing circumferential grooves of micrometer width on both bodies, which represent the alignment of both surface topographies during run-in in order to maximize the real contact area until steady state. In addition flakes as well as delaminations appear (Figures 5a and 6a). According to the backscattered-electron mode (BSE) SEM pictures (Figures 5b and 6b), in which any material being e.g. an oxide would appear darker, there are no tribochemical reaction layers at all.

For the CrMnMoN-steel and the LC-CoCrMo alloy with the smaller steady-state wear rates still circumferential grooves can be seen as a result of the run-in process (Figures 7 and 8). BSE (Figure 7a and 8b) and SE (Figure 7b and 8a) mode SEM figures show a distinct amount of tribochemical reaction layers appearing as dark patches sticking rigidly to the surfaces. In addition delaminations and further small surface cracks are visible for the CrMnMoN-steel. The LC-CoCrMo alloy specimens show nearly no delaminations but indentations beside the tribochemical reaction layers.

3.2 Torsional Fatigue Behavior

The fatigue data were evaluated following standard procedures (Christ, 1991; Suresh, 1989). Thus, the final results are shown here without any details about the cyclic elastic and plastic strain amplitudes of each single stress-strain hysteresis.

3.2.1 Evolution of Equivalent Strains—The equivalent mean plastic strain ϕ_V is plotted versus the mean shear stress τ_m at 25 Hz (Figure 9). ϕ_V represents the sum of all plastic strain amplitudes of the stress-strain hysteresis. During incremental step tests metals show a mostly linear relation between ϕ_V and τ_m at small stress amplitudes while at a certain stress the curve becomes distinctly steeper. The reason for this be either the generation of small cracks, which would lower the stiffness of the sample, or cyclic softening, or both.

The CrNiMo steel is the weakest under such torsional fatigue already showing a cyclic instability at a mean stress of about 70 MPa, while the LC-CoCrMo alloy reaches 220 MPa. Both high-Nitrogen steels show similar values around 160 MPa. If one reduces the loading frequency to 1 Hz (Figure 10) the critical mean stress drops markedly showing a distinct strain rate sensitivity under cyclic shear. Again the CrNiMo-steel is the weakest with about 50 MPa while the other three reach about 140 MPa.

The stress strain behavior below the critical stress level shows that cyclic shear stresses give rise to cyclic plastic deformation (cyclic creep or ratcheting) for all materials already at relatively small stress levels. This is the more pronounced the smaller the strain rates are. The CrNiMo-steel appears to be most prone to this and differs distinctly from all other materials tested.

3.2.2 Fatigue Appearances (TEM)—The specimens were investigated as to their fatigue appearances by means of TEM close to the surfaces in order to evaluate the areas of highest shear stresses.

The CrNiMo steel shows dislocation cells (Figure 11a), which are not as distinct as they have been reported from axial fatigue tests with the same material (Göbbeler, 1998). The reason is that under these incremental step tests the specimens only underwent 90,000 cycles in total and only 5,000 cycles at the highest stress level. Thus, dislocation arrangements are not as pronounced as they would after some millions cycles at usual constant stress or constant strain tests. Still the generation of such cell walls as a result of wavy slip is unequivocal (Li and Laird, 1994). For the CrNiMnMoN steel there seem to be much more planar sliding (Figure 11b) but still some dislocation cells are generated as well. This is known for high-nitrogen steels containing Nickel, 0.06 weight-% C, and up to 0.4 weight-% N (Degallaix et al., 1987; Gavriljuk and Berns, 1999; Vogt et al., 1999; Vogt et al., 1984). A further increase of N-content up to about 1 weight-% like for the Ni-free CrMnMoN steel (Figure 12a) brings about solely discrete sliding with twins, stacking faults, and finally ϵ -martensite. The same appearances hold true for the LC-CoCrMo alloy (Figure 12b) and in a first approximation can be attributed to the low stacking fault energy (Chalant and Remy, 1980; Dillamore, 1970).

4. Discussion

The major aim of this paper is to understand, why there are such marked differences in the wear rate and wear behavior between CrNiMo- and CrNiMnMoN steels on the one side and CrMnMoN steels as well as CoCrMo alloys on the other side even though all of them show the desired nanocrystalline microstructures (Figure 13a for e.g. CrNiMo- and 13b for e.g. CrMnMoN-steel) within the uppermost contact surface. Obviously the major differences can be connected to the distinct difference of wear particle size between the two groups of materials. While the high-wear group shows microsize particles (Figure 1a, 14a) the low-wear group only shows them within the ultrafinecrystalline (100 - 500 nm) or nanocrystalline (< 100 nm) range (Figure 1b, 14b). It is postulated that the microsize particles must have detached from the worn surfaces by different mechanisms than the nanosize ones.

4.1 The Source of Nanosize Wear Particles and their Influence on the Acting Wear Mechanisms

One can assume that because of their predominant size range below 100 nm (Büscher, 2005; Pourzal et al., 2011) and of the fact that this resembles the size of the nanocrystals the nanosize wear particles stem from the tribomaterial. The detachment mechanism is unknown and will be a matter of future research. At this point it is important to notice that for such material the underlying shear zone obviously does not show any crack initiation and propagation below the nanostructured tribomaterial and, therefore, stabilizes it sufficiently. As a result only nanosize particles are generated, which tend to roll between the contacting bodies, because of their small size and compact shape, and lead to nanosize indentations. As a consequence the uppermost material undergoes distinct cyclic plastic straining by multiple indentations. Such appearances have been attributed to a submechanism of surface fatigue (Fischer, 1996; Wimmer et al., 2001; Wimmer et al., 2003). In parallel the contacting metals are separated by tribochemical reaction layers (mechanically mixed and tribooxidation layers) and rolling oxidic wear particles prevent adhesion and abrasion. Thus such combinations of submechanisms of tribochemical reactions (tribooxidation, mechanical mixing) and “third-body” surface fatigue (indentations) provide the capability to allow for mild-sliding wear rates even under dry friction contact conditions as in the presented disc-on-pin test. It has already been shown earlier for CoCrMo alloys that the same acting wear mechanisms would allow for ultra-mild sliding wear also under boundary lubrication (Büscher et al., 2005b; Wimmer et al., 2009).

4.2 The Source of Microsize Wear Particles and their Influence on the Acting Wear Mechanisms

For microsize wear particles the contact situation is totally different because fewer particles are in between the contacting bodies and if at all they might not roll so easily as nanosize ones. Thus they tend more towards sliding and generate grooves. Thus the wear mechanism alters towards abrasion. Because of the shallow attacking angle the submechanisms microploughing and microfatigue prevail (Zum Gahr, 1987). Such submechanisms of abrasion hinder the generation of tribochemical reaction layers as well as remove any existing ones instantaneously. They could even give rise to adhesion under dry contact conditions. As a result of such wear mechanisms high wear rates predominate.

4.3 The Impact of the Subsurface Shear Fatigue Zone

The question is, why these materials produce such large wear particles even though they are much bigger than the maximum thickness of any tribomaterial layer observed so far (Büscher and Fischer, 2005; Büscher et al., 2005a; Büscher et al., 2005b; Pourzal et al., 2009b; Wimmer et al., 2009). Thus any crack initiation and propagation for the wear particle generation must have taken place further away from the contact surface underneath the tribomaterial. This would be within the observed shear zone generated by cyclic shear forces. Looking at the 1 Hz shear fatigue data (Figure 10) it is obvious that the CrNiMo-steel becomes unstable already at 50 MPa while all others show such behavior at a 3times larger mean shear stress. From this one could easily derive that the shear fatigue zone is likely to become mechanically unstable e.g. by microcracks (Kirk and Swanson, 1975; Mughrabi, 2009) or shear bands (Rainforth et al., 1992) at relatively small cyclic stresses.

Still this would yet not explain the distinct difference between the two groups of materials derived from the wear tests. If the shear fatigue properties at 1 Hz (Figure 10) would be predominant the CrNiMnMoN steel, which belongs to the high wear group, should show a wear rate as small as the CrMnMoN steel and the CoCrMo alloy. Now we know that any friction force comes with superimposed higher frequencies induced from frictional contacts. Thus we could make account to the 25 Hz fatigue data in order to distinguish the different

fcc materials further (Figure 11). Again it would separate CrNiMo from CoCrMo. But it would not render any distinct difference for the two high-nitrogen steels. From this we can conclude that this simple stress-strain criterion alone does not explain the differences of the wear behavior.

Looking at the microstructures after shear fatigue tests it becomes obvious that both steels of the high wear group show either a distinct (CrNiMo, Figure 11a) or at least a tendency (CrNiMnMoN, Figure 11b) toward wavy slip behavior, while the other two (Figures 12a, 12b) solely show planar slip. Interestingly enough this marked difference between the high wear and low wear group of materials is also true for the shear fatigue zone after the wear tests (Figure 16)

4.4 The Influence of the Slip Characteristics under Shear Fatigue

In order to relate the difference of wavy and planar slip under shear fatigue to the overall wear behavior one can make reference to the model of Saleski et al. (Saleski et al., 1983), who showed a dislocation cell based detachment mechanism under sliding wear. According to this such cell formation leads to a localization of strains, based on the fact that inside the cells the material is free of dislocations - similar to a recovered state - and, therefore, free of strains. Now crack initiation and propagation are likely within the cell walls or at the interface between areas with cell walls and the underlying deformed base material because of the localized extreme strain gradients. In addition cell walls block dislocations so that they become immobile. The strength certainly increases by the inverse size of the cells themselves and the density of still mobile dislocations in between them. But simultaneously ductility decreases. Thus fatigue cracks initiate at and propagate along such dislocations cells (Suresh, 1989). Under planar slip dislocations, twins, stacking faults, and ϵ -martensite remain mobile, but only on their discrete sliding planes. Thus even if the lattice defect density and, therefore, the strength increases within the shear fatigued zone, mechanical instabilities e.g. like shear bands, crack initiation and propagation do take place at distinctly higher stress or strain levels.

In summary it appears that those metals, which allow for the generation of a dislocations cell substructure will undergo crack initiation and propagation within the shear fatigue zone. Thus wear particles are generated in a distance of some μm below the surface, which automatically leads to a much larger size compared to those detaching from the tribomaterial. Since large particles are few and not able to roll within the contact area they lead to large contact stresses or even grooving. Such proposed sequence of microsize particle generation still stabilizes itself at a high steady-state wear rate giving rise to abrasion (grooves in Figures 5, 6) with its submechanisms microploughing and microfatigue. Adhesion might take place as well with very large particles (flakes in Figures 5, 6). Tribochemical reaction layers, which would prevent adhesion, do not develop at all. In contrast to this nanosize particles allow for much more contact spots and consequently orders of magnitude smaller contact stresses. In addition they can roll easier leading to nanosize indentations which bring about surface fatigue on the nanometer scale and even under dry friction allow for the additional generation of tribochemical reactions layers (Figures 7, 8).

4.5 Importance for Biomedical Applications

Most of our understanding about wear and particle formation of metallic implants is based on empirical data. This is dangerous because without a mechanistic perception of the wear principles it is difficult to transfer results of a certain material from one tribological system to another. Most recently, this deficit has become obvious with metal-on-metal articulations triggering adverse soft tissue reactions, including pseudotumors (Catelas and Wimmer,

2011), when THA implants with large head sizes were designed based on available clinical data of implants with small head sizes. Various manufacturers relied on the success of small diameter MoM hip joints without knowing the specific tribological effects of certain design parameters - and failed. One aspect, which has been overlooked by many, is the importance of alloy microstructure in this respect.

In this study, we have laid the factual groundwork of the interaction of microstructure and wear and discussed the importance of cyclic creep in the context of particle formation. Applying this new understanding to classic biomedical materials, we were able to explain success and failure of cobalt-chromium and stainless steel in tribological applications. With this new knowledge we expect that it will be possible to screen and metallurgically improve metallic candidate materials regarding their capability to generate ultra-mild wear in self-mating bearing applications.

5. Conclusion

The comparison of the metallic materials investigated under shear fatigue and mild sliding wear shows that CrNiMo steels are different from CoCrMo alloys for metallurgical reasons.

Microsize particles are produced by crack initiation and propagation within the shear fatigue zone which is related to the formation of subsurface dislocation cells and, therefore, by the fact that the CrNiMo solid solution allows for wavy-slip.

These microsize wear particles bring about abrasion with its submechanisms microploughing and microfatigue and prevent tribochemical reactions while nanosize wear particles lead to surface fatigue in the nanometer range and allow for tribochemical reactions.

The Ni-containing austenitic steels have distinctly higher wear rates under dry friction than the Ni-free high-nitrogen steel and LC-CoCrMo alloy. This is mainly related to the acting wear mechanisms and their submechanisms, which depend on the size of wear particles.

The addition of e.g. 0.4 weight-% of N into a Ni-containing CrNiMo solid solution might improve the fatigue properties but does not improve the wear behavior, because this does not fully suppress wavy-slip.

In contrast to this a Ni-free CrMnMo solid solution with further additions of C and N of up to 1 weight-% only shows planar slip within the shear fatigue zone, which distinctly improves the wear behavior. Still it does not fully achieve that of CoCrMo, which also shows solely planar-slip behavior.

The most important outcome of this investigation is that ultra-mild sliding wear rates under dry and boundary lubrication conditions in self-mating contacts can be achieved with those metals, which do not allow wavy-slip within the shear zone underneath the nanocrystalline tribomaterial. This explains why 316L-type of steel failed in such tribosystems.

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Figure 1.
Wear Particles from Self-Mating Steel Couples after Dry Sliding Wear according to (Büschler, 2005)

Figure 2.
Scheme of the Subsurface Microstructures under Mild- and Ultra-Mild Sliding Wear based on Schmalz' original Figure of 1936 and extended by (Büschler, 2005) on the Basis of Retrieval Analyses.

Figure 3.
Microstructures of Solution Annealed Materials Investigated Prior to Testing

Figure 4.
Wear Rates W over Wear Path L

Figure 5.
Wear Appearances on the Worn Surfaces of the CrNiMo Steel Couple after 5 km Wear Path depicting Grooves, Delaminations, and Flakes.

Figure 6.

Wear Appearances on the Worn Surfaces of the CrNiMnMoN Steel Couple after 5 km Wear Path depicting Grooves, Delaminations, and Flakes.

Figure 7.
Wear Appearances on the Worn Surfaces of the CrMnMoN Steel Couple after 10 km Wear Path depicting Tribochemical Reaction Layers and Delaminations

Figure 8.
Wear Appearances on the Worn Surfaces of the CoCrMo Couple after 12 km Wear Path depicting Tribochemical Reaction Layers and Indentations.

Figure 9.
Development of Mean Equivalent Cyclic Plastic Strain over Mean Shear Stress in Torsional Incremental Step Fatigue Tests at 25 Hz and $R = 0.1$

Figure 10.
Development of Mean Equivalent Cyclic Plastic Strain over Mean Shear Stress in Torsional Incremental Step Fatigue Tests at 1 Hz and $R=0.1$

Figure 11.
TEM Figures of Shear Fatigued Ni-containing Steels

Figure 12.
TEM Figures of Shear Fatigued Ni-free Steel and Co-base Alloy

Figure 13. Nanocrystalline Metal directly at the Contact Surfaces for the CrNiMo- and the CrMnMoN-Steel Couples. The Arrow points to the Contact Surface.

Figure 14.
Wear Particles from Self-Mating Steel and LC-CoCrMo Couples after Dry Sliding Wear

Figure 15. Deformation Appearances within the Subsurface Shear Zones of the CrNiMo- and the CrMnMoN-Steel Couple.

Table 1

Alloy Designation of Materials Tested and Hardness after Solution Annealing prior to testing

Material (Group)	Standard Designation	Material-Number and/or Brand Name	Solution Annealing under 98%Ar+2%H ₂	Hardness HV10
X5CrNiMo17-13-2 (CrNiMo Steel)	DIN ISO 5832-1 ASTM F138 – 00	1.4441 316L	30 min/1050°C/H ₂ O	266±6
X6CrNiMnMoN22-10-4-3 (CrNiMoN Steel with 0.4 % N)	DIN ISO 5832-9	REX734		290±10
X13CrMnMoN18-14-3 (CrMnMoN Steel with 0.9 % N)	≈ ASTM F2229 – 02	1.4452 P2000	30 min/1150°C/H ₂ O	270±12
CoCr29Mo6 (CoCrMo Alloy)	DIN ISO 5832-6 ASTM F1537– 00	LC-CoCrMo		340±28

Table 2

Disc-on-Pin Test Parameters

Body (upper)	Counterbody (bottom)	Interfacial Medium	Environment
	Disc	Pin with 16 mm tip radius	-	Laboratory Air of 40 % rel. humidity
Normal Force in N	5	Max. Hertzian Pressure in MPa	370	at start of test
Relative Velocity in m/s	0.1	Ambient Temperature in °C	25°C	