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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.

Keywords

CoCrMo alloy; metal-on-metal; hip prosthesis; hard phases; carbide; precession electron diffraction

1. Introduction

During the last 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,

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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 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 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 hr 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 hr, 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

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 + 4g K₂S₂O₅ 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. Any indentations at the phase boundaries were discarded. The average hardness and standard deviation are reported.

TEM thin foils were prepared using an FEI Helios dual beam focused ion beam (FIB). A protective platinum layer was coated on the region of interest, and a rectangle of 20 µm × 2 µm × 6 µm was cut out with a gallium ion beam at 30 kV. The thin piece was then attached to an Omniprobe TEM grid, followed by thinning to ~100 nm with 5 kV ions. A Hitachi HD2300 TEM/STEM equipped with an energy dispersive X-ray spectrometer (EDS) operated at 200 kV was used for elemental mapping.

A JEOL 2100F TEM operated at 200 kV was employed to identify the crystallographic structure by examining either select area diffraction (SAD) or nano-beam diffraction (NBD) patterns. These two techniques, however, involve strong dynamical diffraction particularly for thick specimens. As a result, diffraction intensities are usually different from what is predicted by the kinematical theory, which significantly complicates the analysis. In order to ease the solutions of structure, we used precession electron diffraction (PED) (Vincent and

Midgley, 1994), to obtain pseudo-kinematical patterns. Figure 1 shows a diagram of the PED system at Northwestern University. The system generates a serial conical illumination rocking on the area of interest, combining a complementary post-specimen descanner bringing spinning diffraction beams to spots. The semi-cone angle was set to 23.7 mrad. Detailed information of the setup has been described elsewhere (Own et al., 2005). Because the Bragg reflections are collected in off-zone conditions, dynamical scattering is greatly reduced. For reference, the PED method is relatively new and has proved to be a very powerful approach to obtaining crystallographic information within a transmission electron microscope, in most cases rather superior to older fixed-beam diffraction techniques. For some recent publications see (Ciston et al., 2008; Gemmi et al., 2010; Gjonnes et al., 1998a; Gjonnes et al., 2004; Gjonnes, 1997; Gjonnes et al., 1998b; Hadermann et al., 2010; Hadermann et al., 2011; Meshi et al., 2011; Moeck and Rouvimov, 2010; Own et al., 2006a; Own et al., 2006b; Rauch et al., 2010; Schurmann et al., 2011; Sinkler and Marks, 2010; Sinkler et al., 2007).

3. Results

3.1 Cast Alloy

Figure 2a shows an optical micrograph of the head component made from the as-cast alloy. The specimen had typical lamellar hard phases (as we will see later they are mixtures of fine hard phases rather than single phase carbide) of $\sim 50 \mu\text{m}$ in length within the grains and at the grain boundaries. These hard phases have a similar appearance to those reported in Refs. (Caudillo et al., 2002; Dobbs and Robertson, 1983; Lopez and Saldivar-Garcia, 2008; Montero-Ocampo et al., 1999; Saldivar-Garcia and Lopez, 2005). Several pits were observed inside the hard phases, which were presumably formed during the mechanical polishing and/or etching. The cup component, also made of the as-cast alloy, had grain boundaries with a typical grain size of a few millimeters, as shown in Figure 2b; the inset shows an SEM micrograph of a hard phase at a higher magnification. The hard phases in the cup component were on the order of $5 \mu\text{m}$, smaller than those in the head component, and were found mostly within the grains with straight phase boundaries. Pits were also observed in the cup component.

TEM specimen preparation of a hard phase from the head component is illustrated with the SEM micrographs in Figure 3. (For completeness, we note that the hard phase was protected by a $\sim 2 \mu\text{m}$ thick platinum layer during sample preparation.) Figure 4a shows a TEM micrograph of the hard phase from the head component. Interestingly, it was composed of very fine grains of about 100 nm. Figure 4b shows a phase boundary between the matrix and carbides, which was found to be a few nanometers thick. A number of stacking faults (which show classic fringe contrast in a TEM image) were present in the matrix. Figure 4c shows a typical electron diffraction pattern of an individual nm-size grain taken along the [01-1] zone axis. The nanophases have a cubic structure with a lattice parameter of 1.092 nm, which is likely to be M_{23}C_6 -type carbide; but this is not definitive. The carbides of the cup component, despite appearing smaller, are similar to those in the head component and feature $\sim 100 \text{ nm}$ nanograins, see Figure 4d.

As stated previously, it is complicated and somewhat dangerous to solve crystal structure using regular SAD/NBD diffraction due to the strong dynamical diffraction of electrons. We therefore used PED with either parallel nano-beam or converged beam illumination. Figure 5a and 5b show PED converged beam electron diffraction (CBED) and spot diffraction patterns of typical nanograins near a [011] zone, respectively. The integration over incident directions makes the pattern appear to be at the zone axis, a well-established effect. A simulated Cr_{23}C_6 carbide pattern based on kinematical theory is shown in Figure 5c. The intensities of the PED patterns can be readily compared to the simulated patterns as expected

(Gjonnes, 1997; Own et al., 2006b), for example the {04-4} and {33-3} diffractions display relatively strong intensity while {02-2} and {11-1} are dim. It is evident that the grain is $M_{23}C_6$ -type carbide. While most of the nanograins were determined to have a $M_{23}C_6$ -structure, a few fcc nanophases similar to the matrix were also observed in the hard phases.

Figure 6 shows a bright-field TEM micrograph of the carbide from the head component along with the corresponding elemental mappings (Co, Cr and Mo). The chemical composition of the nanograins in the carbides varied significantly, indicating poor homogeneity of the mixed hard phases even for grains having the same $M_{23}C_6$ crystallographic structure. The compositions of regions 1–4 labeled in Figure 6b are listed in Table 1. In general, the nanograins were compositionally divided into two categories: some grains contained a relatively high Co content, while the others were Cr-rich.

3.2 Wrought Alloy

Figure 7 shows an optical micrograph of the wrought alloy. The matrix grain size was a few microns, with $\sim 1 \mu\text{m}$ large carbides distributed uniformly within the grains and at the grain boundaries. The TEM micrograph in Figure 8a shows that the internal carbide structure is homogeneous. Based on the electron diffraction pattern in Figure 8b, it was determined that these carbides are of $M_{23}C_6$ -type with a lattice parameter of 1.066 nm. The chemical composition of the carbide in the wrought alloy was measured by EDX to be $\text{Co}_{14}\text{Cr}_{72}\text{Mo}_{14}$ (in wt.%) with error of about 1%.

Localized hardness and modulus of both the mixed hard phases and homogeneous $M_{23}C_6$ carbides were measured using nanoindentation. Despite the differences in the microstructural appearance, the mechanical properties of the mixed hard phases in the head and cup components made of as-cast alloy were similar. This is not surprising, as both carbides were composed of nanograins. Figure 9a and 9b show AFM micrographs of the hard phases in the cast alloy head component and the wrought alloy after indentation tests. Typical force-displacement curves are shown in Figure 9c. The hardness and modulus were determined using the Oliver-Pharr model, by fitting the unloading curves using the power law (Oliver and Pharr, 1992):

$$P = C(h - h_f)^m$$

where h_f is the maximum depth after unloading and C and m are material constants (Oliver and Pharr, 1992). The hardness and modulus of the hard phase mixture in the cast alloys were determined to be $15.7 \pm 0.9 \text{ GPa}$ and $269 \pm 6 \text{ GPa}$, respectively. The hardness of the matrix in the cast alloy was $6.4 \pm 0.3 \text{ GPa}$. For comparison, the hardness and modulus of the carbides in the wrought alloy were $30.7 \pm 2.6 \text{ GPa}$ and $309 \pm 16 \text{ GPa}$, respectively, whilst the hardness of the wrought alloy's matrix was $9.4 \pm 0.8 \text{ GPa}$. The carbides in the wrought alloy are nearly twice as hard as those of the mixed hard phases in the cast alloy. It can be seen from the unloading curves in Figure 9c that the carbides in the wrought alloy underwent less plastic deformation than the mixed hard phases in the cast alloy.

3.3 Microstructures Cooled at Different Rates

The detailed heat treatments of the cast retrieval and the wrought alloy were not available, which limits understanding of why the different microstructures arise. In order to unravel the origin of the different carbide phases, the wrought alloy was remelted and cooled at either $50 \text{ }^\circ\text{C/s}$ or $0.2 \text{ }^\circ\text{C/s}$. Figure 10a shows an optical image of the specimen cooled at $0.2 \text{ }^\circ\text{C/s}$. Blocky hard phases were observed to be $\sim 200 \mu\text{m}$ long and $\sim 15 \mu\text{m}$ wide. A TEM micrograph of the hard phase made using FIB is shown in Figure 10b. The phase is

composed of ~100 nm fine structures, similar to the mixed hard phases in the as-cast alloy, and the chemical compositions of the nanostructure varies for each nanostructure. The chemical compositions of area 1 (Cr rich) and 2 (Mo rich) are listed in Table 2.

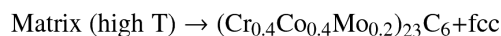
An optical micrograph of the hard phases in the specimen cooled at 50 °C/s is shown in Figure 11a. The carbide phases were 5–10 μm single phases, see Figure 11b. Table 2 shows the chemical compositions of the single phase carbides, which contained more Mo (23.16%) than the matrix (6.87%).

The hardnesses of the mixed hard phase and the matrix of the specimen cooled at 0.2 °C/s were 15.7 ± 9 GPa and 6.4 ± 3 GPa, respectively, which are close to those of the cast retrieval. For the specimen cooled at 50 °C/s, the hardness is 16.3 ± 0.9 GPa for the single phase carbide and 6.2 ± 0.3 GPa for the matrix. The mechanical properties of the hard phases are summarized in Table 3.

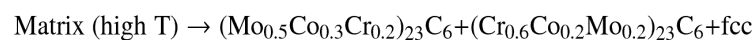
4. Discussion

$M_{23}C_6$ carbides are the dominant hard phase in both cast and wrought CoCrMo alloys. Transformation from $M_{23}C_6$ to M_6C , as suggested by Clemow and Daniell (1979), was not observed. Although the carbides investigated in this study have the same $M_{23}C_6$ -type crystallographic structure, they exhibited different structural and mechanical properties. The mixed hard phases found in the head component made of the cast alloy appeared to be blocky (~50 μm) with an elongated morphology, while those found in the cup component appeared to be on the order of a few microns. Despite the smaller size in the cup component, the mixed hard phases in both head and cup were mixtures of three phases, i.e. the fcc phase similar to the matrix, Co-rich $M_{23}C_6$ carbide, and Mo-rich $M_{23}C_6$ carbides. The two kinds of carbide have similar nanohardnesses of about 15.7 GPa. The carbides in the wrought alloy, on the other hand, were a few microns large $M_{23}C_6$ single phases. This is consistent with the electron microprobe measurements, in which wrought alloys exhibited a higher degree of homogeneity than cast alloys (Devine et al., 1972). Clemow and Daniell (1979) measured the chemical compositions and reported little Mo segregation (variation < 2%) across cast alloys. Therefore the Mo-rich $M_{23}C_6$ carbide in the mixed hard phase should not be due to segregation during casting.

Our hypothesis is that a single phase $M_{23}C_6$ carbide is metastable and precipitates during fast-cooling:



where the compositions used are based upon the EDS results shown earlier for the fast-cooled alloy. A mixed hard phase consisting of crystallographically-identical but chemically-different $M_{23}C_6$ carbides is thermodynamically stable. However, the precipitation of the mixed hard phase is sluggish and only occurred with a slow-cooling rate:



and the compositions are again based upon the earlier EDS results for the slow-cooled alloy. We note that annealing of these samples at 1230 °C for 1hr coarsened the two carbides but did not change the compositions which implies that these are thermodynamically stable. They are also consistent with the retrievals made from a cast alloy. It has been shown that $M_{23}C_6$ has a lower Gibbs free energy than Cr_{23}C_6 below 700 °C (see Table 3 in Ref (Senior, 1988)), and Mo partitioning in $M_{23}C_6$ took place during aging of CrMoV steels

(Senior, 1988). In fact, $M_{23}C_6$ carbides frequently coexist with either M_3C (Senior, 1988) or M_6C carbides (Kuo and Jia, 1985) in annealed CrMoV steels, which is consistent with sluggish kinetics. We note that for the somewhat similar CrMoV steels a large scatter of precipitate compositions and structures have been reported (Senior, 1988) which is consistent with variations due to slightly different annealing treatments. This is also consistent with the scatter in results for the CrCoMo system mentioned in the introduction.

The hardness of the carbide in wrought alloy was about twice that of the cast alloy. Devine and Wulff reported that wrought alloys had better mechanical properties and resistance to crevice corrosion (Devine et al., 1972). The yield strength of the wrought alloy was 689 MPa compared with 551 MPa for cast alloys, whereas the total elongation of wrought alloy was 26% compared to 8% for the cast alloy (Devine et al., 1972). It is worth noting that the influence of hard phases is complicated as sliding wear is determined by many metallurgical properties simultaneously such as hardness, ductility, modulus, etc. (Zum Gahr, 1987). It has been reported that hard carbides promote the strength and resistance against abrasive wear (Antony, 1983; Gomez et al., 1997; Pourzal et al., 2009), thus the wrought alloy is expected to be stronger as its $M_{23}C_6$ carbide precipitates are harder than the mixed hard phases in the cast alloy. The SEM micrographs in Figure 12a and 12b show the cross-section of the retrieved implant made of the cast alloy. Fracture of the coarse mixed hard phases near the surface or phase boundary cracks was frequently observed, while no discernible fracture occurred in the matrix. For comparison, the single phase carbides in a wrought alloy tests remained intact after 5 million cycles simulator tests, see Figure 12c. It is clear that the fracture of the coarse carbides consisting of nanograins in the cast metal hip implant should be avoided.

In addition to the mechanical performance of the hip implants, bioreactive particulate CoCrMo nanoparticles generated during the wear processes are of concern recently as they have been associated with adverse local tissue responses (Jacobs et al., 2009). While the nanoparticles may originate from the nanocrystalline layer at CoCrMo alloy surfaces formed via large plastic deformation and dynamical recrystallization as shown by Buscher and Fischer (2005), the mixed hard phases observed in cast alloys may serve as additional nanoparticle sources. Doorn et al. (1998) isolated metal particles from tissues and reported that the particle size ranged from 20–834 nm with the median of 81 nm. The particle sizes and geometry were similar to the nanograins observed in the cast alloy carbides. Wimmer et al. (2001) showed that carbide/carbide contacts under high local stress could result in carbide fracture and spalling out from the surfaces. As showed in the schematic in Figure 13, sliding on the protruded mixed hard phases may lead to the detachment of the nanograins, producing loose nanoparticles. As noted in the optical images, pitting occurred frequently at the mixed hard phases in cast specimens, indicating that nanograins could be spalled out. In simulated tests, Catelas et al. (2003) observed roughly twice as many wear metal nanoparticles of ~53 nm from cast alloy bearings compared to wrought alloy bearings; this may be partly due to the nanograins spalling out as well. Thus, it may be of interest to eliminate the mixed hard phases for CoCrMo alloys used for implants. It is worth noting that the mixed hard phases may not be distinguishable from a $M_{23}C_6$ single phase carbide by XRD alone, since the most of the nanograins have similar $M_{23}C_6$ lattice structures.

One final point of discussion: it should be clear that while the different formation processes (cast versus wrought) produce similar materials, they are certainly not the same and one should expect some differences during use in-vivo because of different load-bearing, wear and friction (when there is no triboactive lubricant graphitic layer (Liao et al., 2011)) during use. Indeed, just describing the material as "cast" or "wrought" is not really correct, as it is very firmly established that fine details of heat treatments in alloys can lead to large changes in microstructure and properties. This clearly shows up in our comparison of the alloys fast-

and slow-cooled. For instance, with high performance alloys used in the aerospace or automotive industries almost every step of heat treatments is precisely controlled, rather than just specifying bounds for the composition as in the current ASTM standards for Co-based alloys for implants. Hence the fact that our results do not completely match what has been reported by others and the fact that variations have been reported in the literature is to be expected, when there are alloys with the same nominal composition without full microstructure control. The varied microstructures may consequently lead to scattered wear rates as well as variable performance of hip replacements in-vivo or in simulated tests (Chan et al., 1999; Streicher et al., 1990). A critical treatment of the microstructure is imperative.

5. Conclusions

In the cast retrieved implant, the size of the mixed hard phases was $\sim 50 \mu\text{m}$ in the head component and $\sim 5 \mu\text{m}$ in the cup component. Hard phases composed of nanograins were found in both head and cup components. PED results show that the hard phases in the cast alloy consists of mostly M_{23}C_6 -type carbides and few fcc phases. The chemical compositions varied from grain to grain. In general, the nanograins were either Co-rich or Cr-rich. The origin of the mixed hard phases was related to slow cooling during solidification. In contrast, the hard phases in the wrought condition were homogeneous M_{23}C_6 single phase. Nanoindentation measurements showed that the hardness of mixed hard phases was $\sim 15.7 \text{ GPa}$, only half that of the homogeneous carbide ($\sim 30.7 \text{ GPa}$) in the wrought alloy. It is suggested that the hard phases consisting of nanograins are detrimental to both wear performance and biocompatibility.

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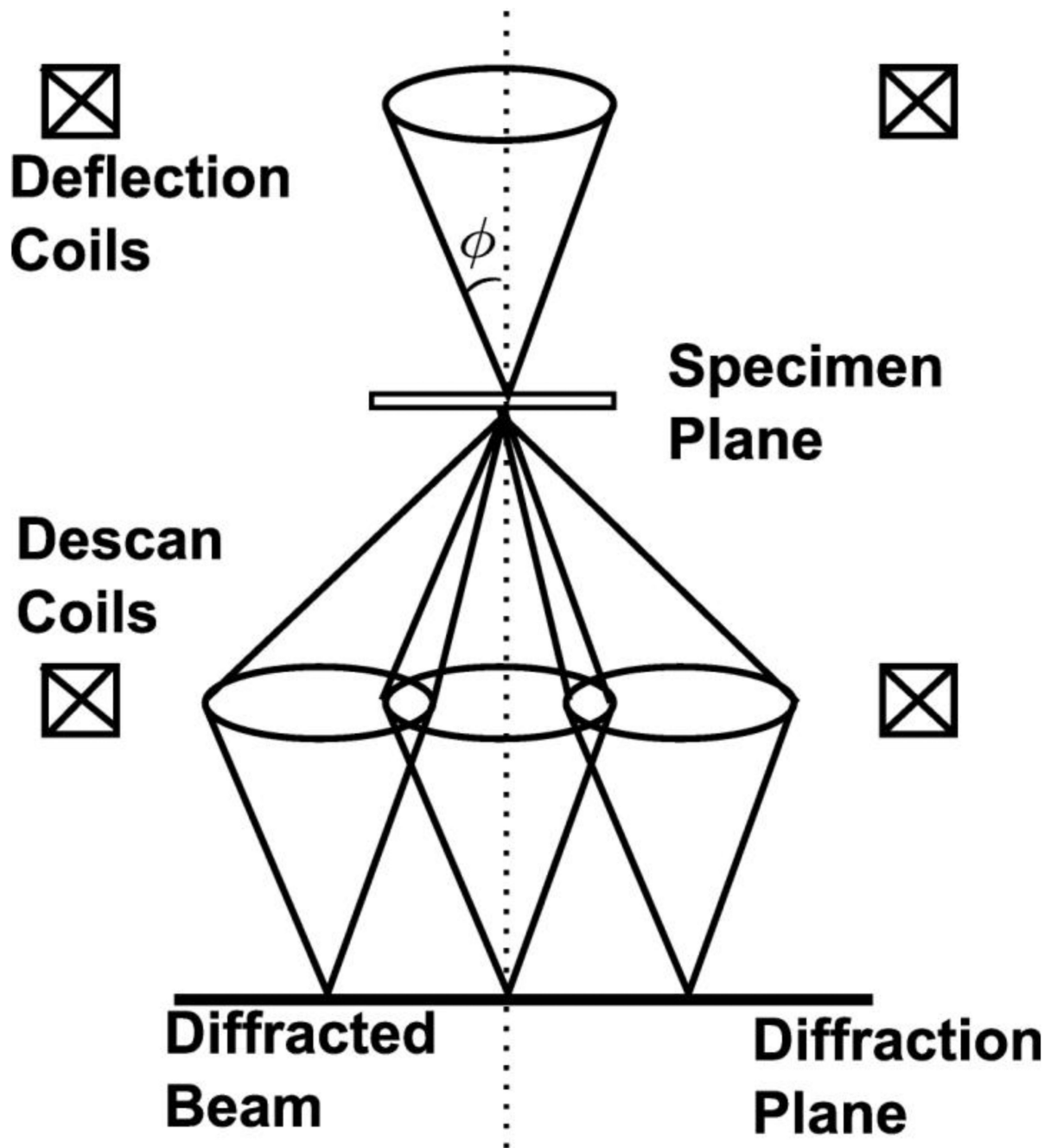


Figure 1.
Simplified schematic of precession geometry. Modified from (Own et al., 2006a).

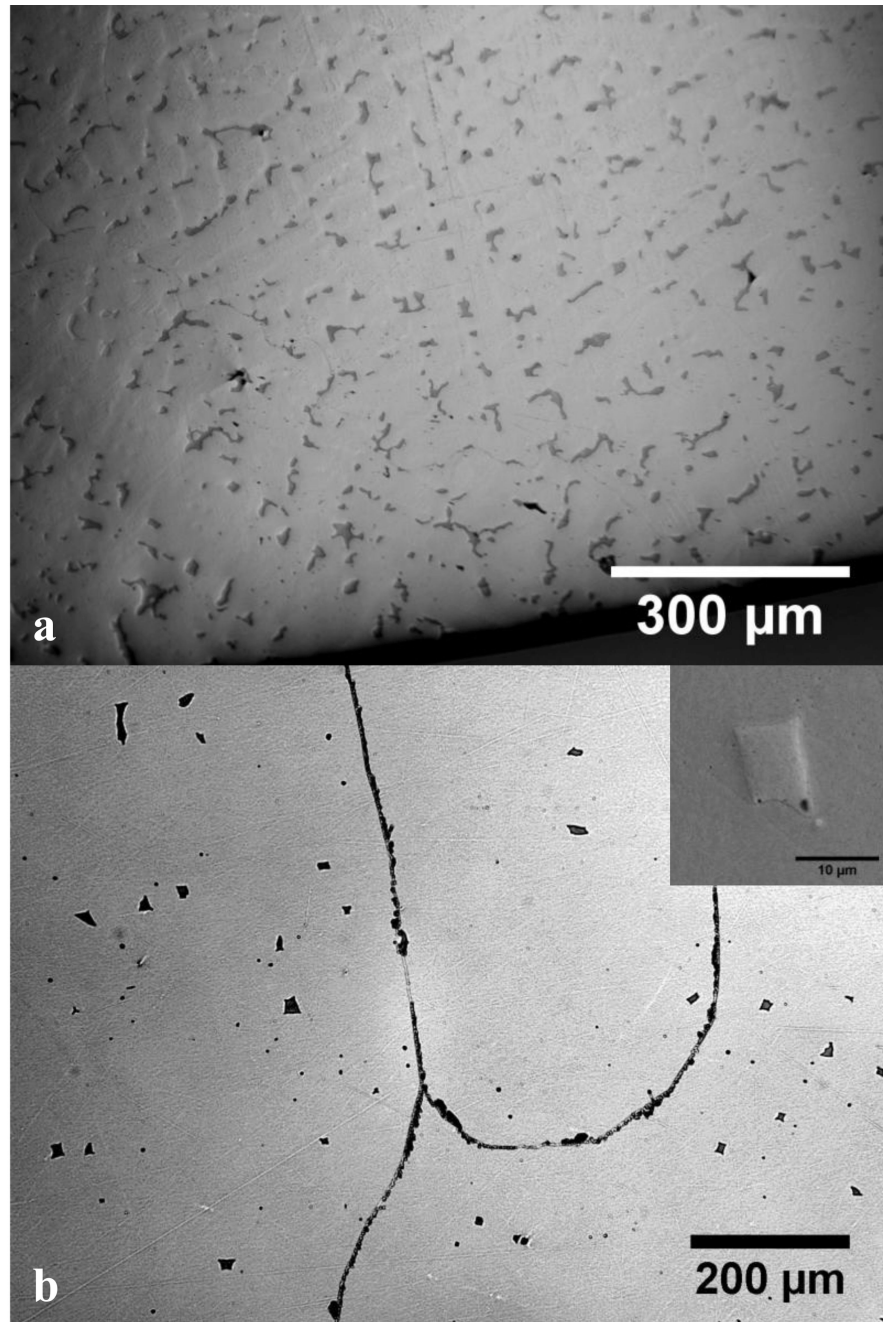


Figure 2. Optical micrograph of the (a) head and (b) femoral cup made of the cast alloy. The inset in (b) is a SEM image at higher magnification of a hard phase region within the cup.

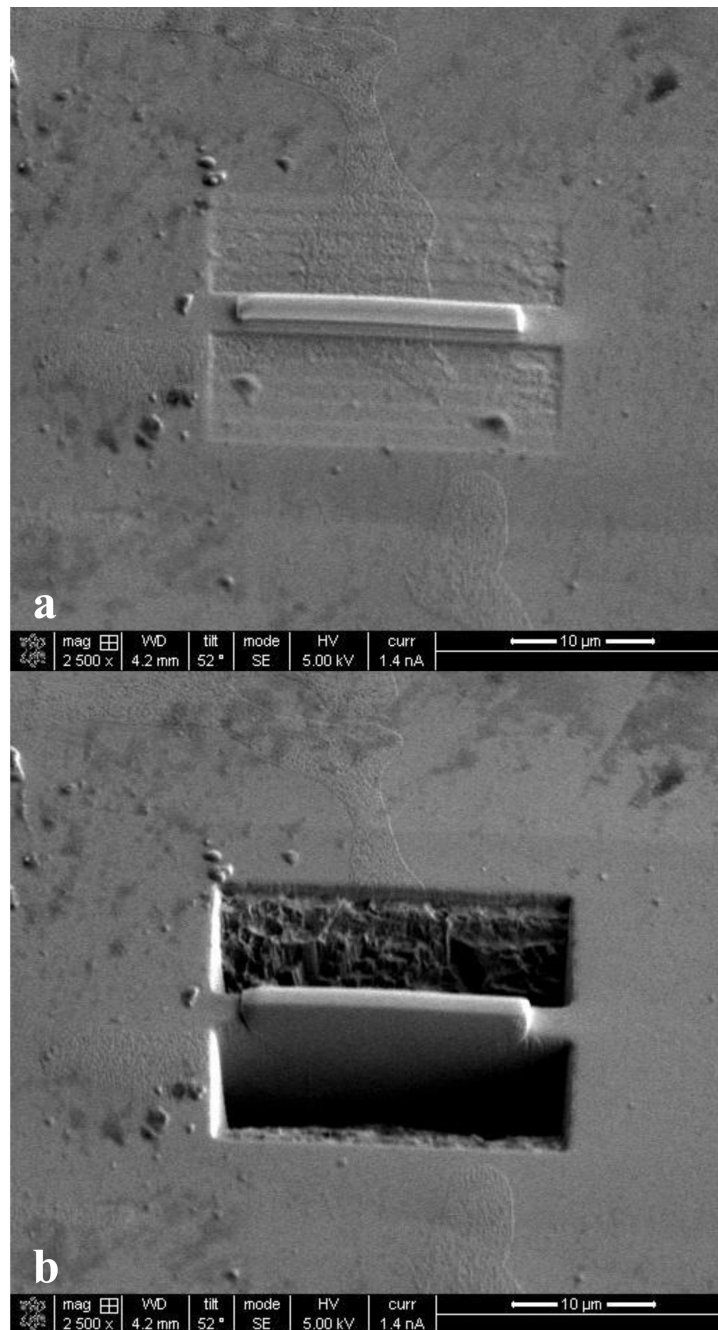


Figure 3. SEM image of preparation of a TEM specimen of a hard phase from the head component. (a) A platinum layer $\sim 2 \mu\text{m}$ thick was deposited on the phase and (b) a thin foil was cut using a gallium ion beam.

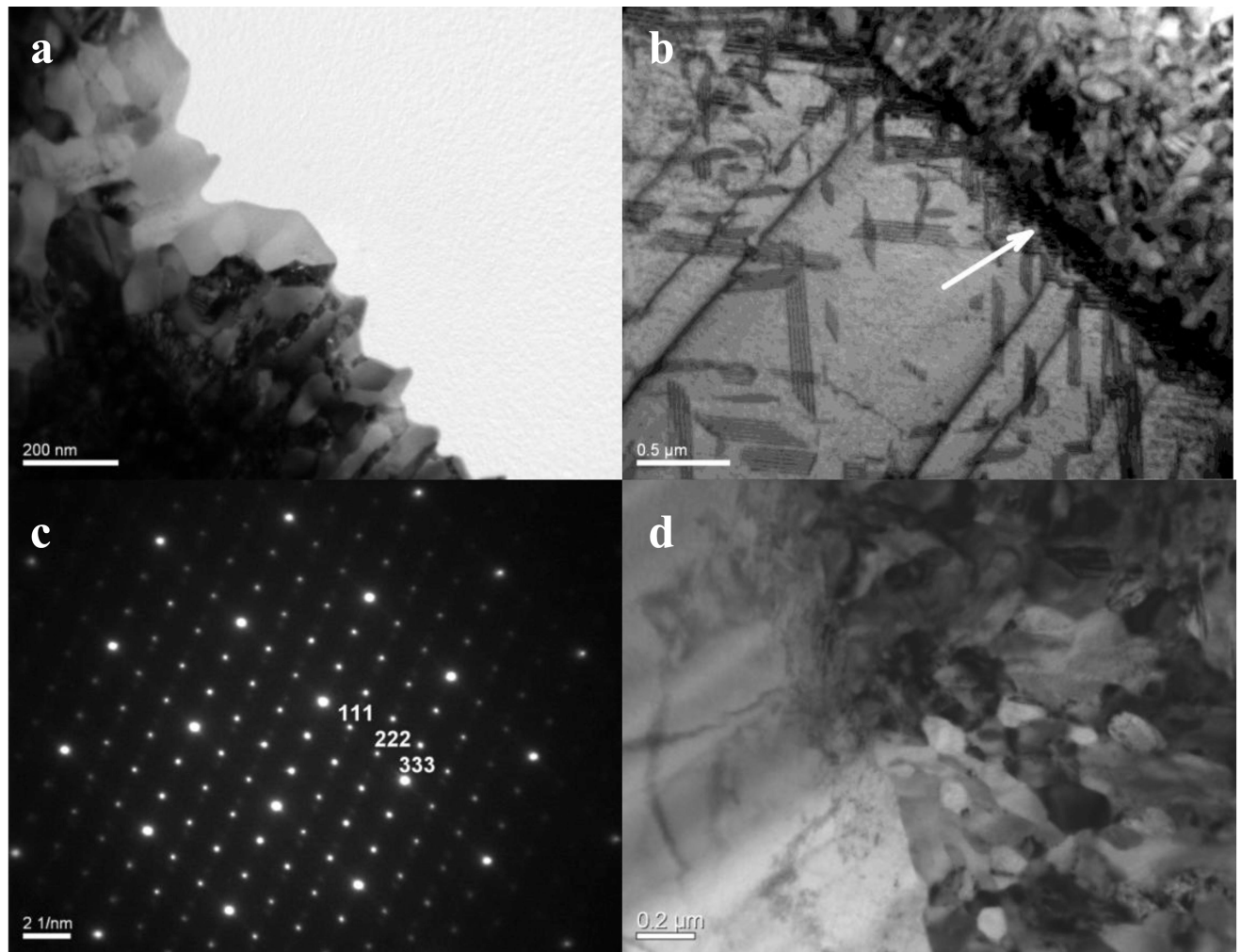


Figure 4.

Bright-field TEM micrographs of (a) the hard phase within the head component of the cast alloy showing nanograins, and (b) the phase boundary (arrowed) of the CoCrMo matrix and hard phases. Stacking faults with standard fringe contrast were present in the matrix. (c) Electron diffraction pattern of a single nanograin along the [01-1] zone axis. (d) The hard phase within the cup component is also composed of nanograins.

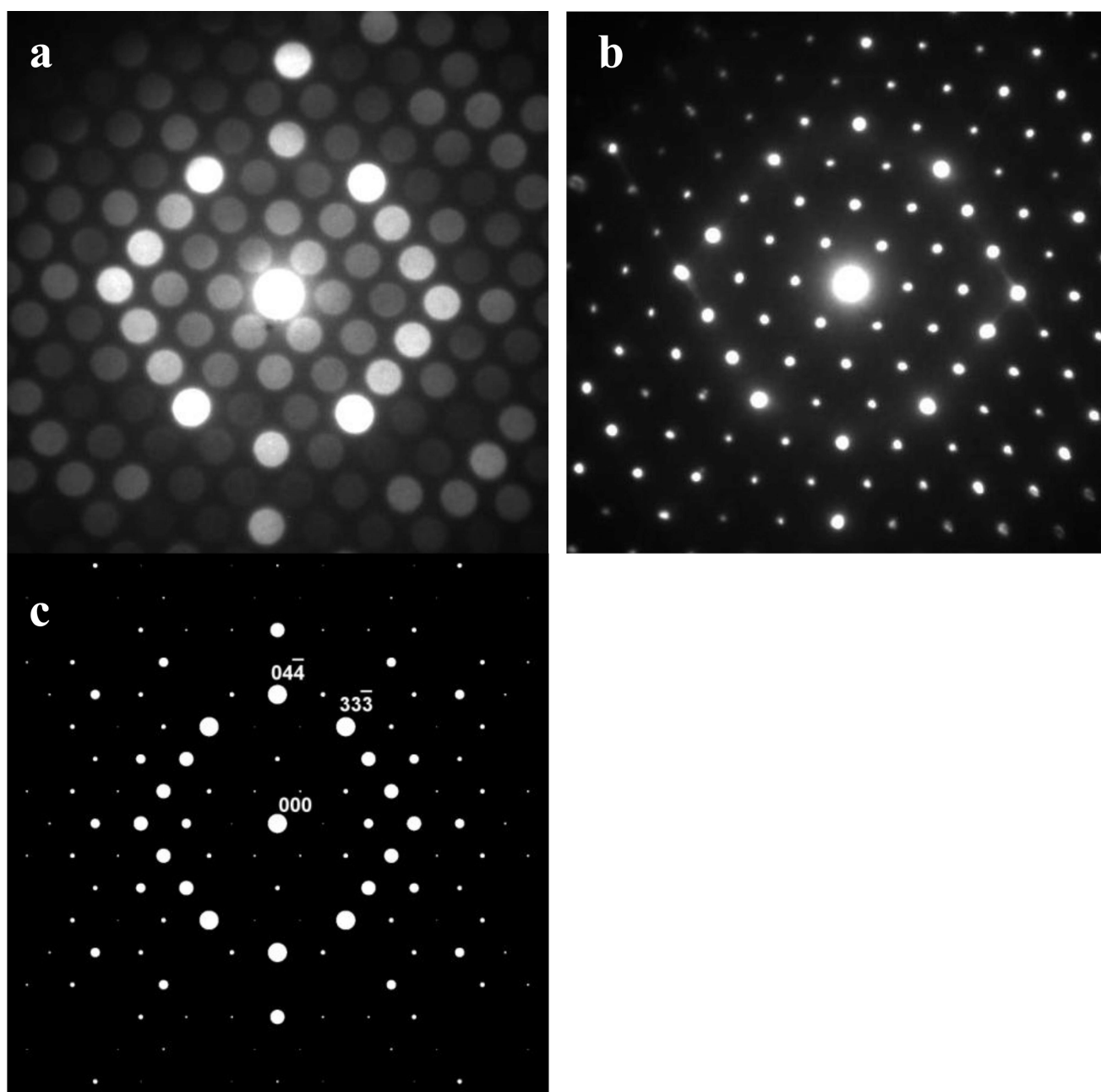


Figure 5.
(a) Precessed CBED pattern and (b) spot diffraction pattern; the zone axis is near $[011]$. (c) Simulated kinematical diffraction pattern.

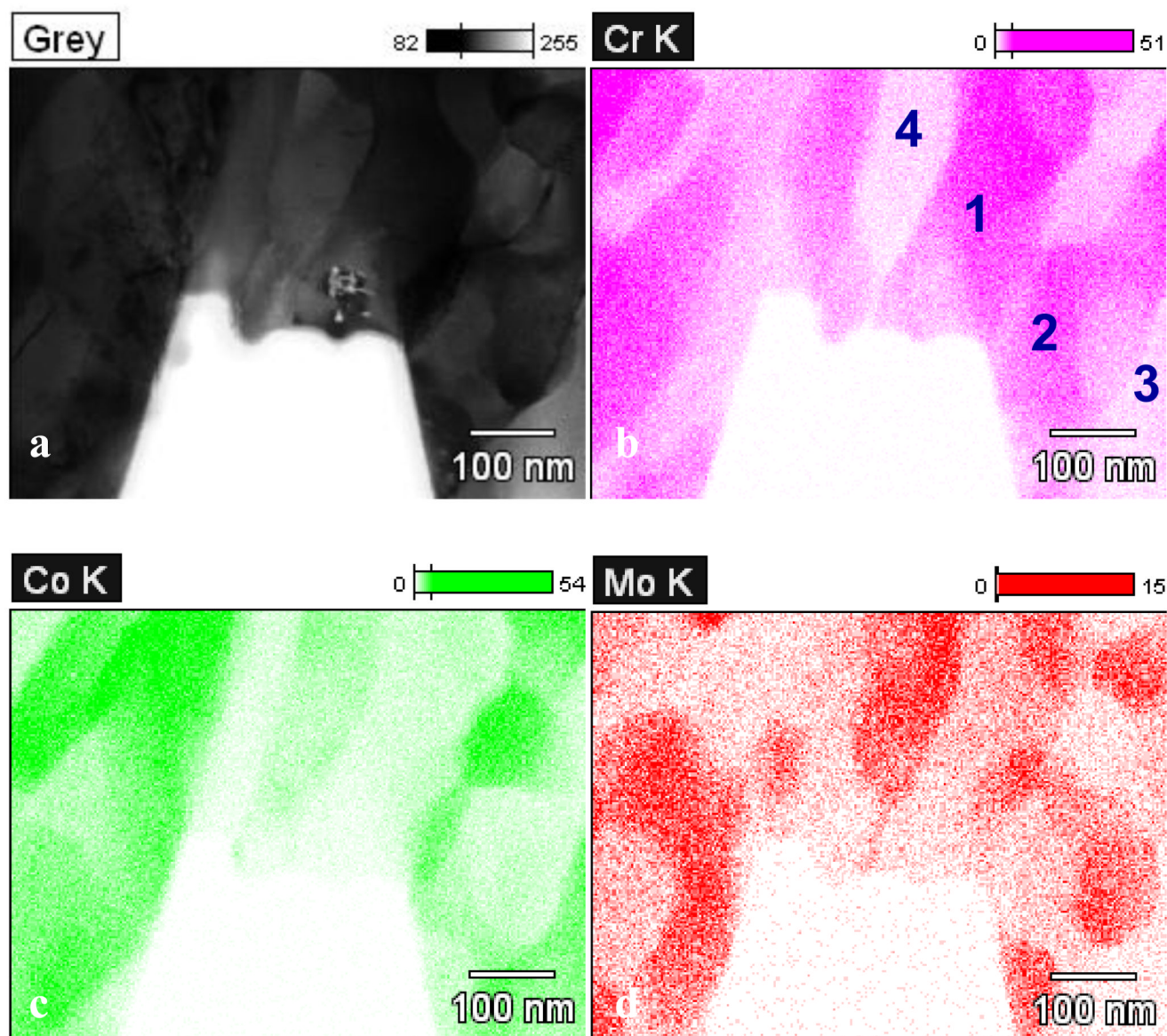


Figure 6.

(a) Bright-field image of mixed fine structures in the cast alloy. (b) Cr, (c) Co and (d) Mo elemental mapping using EDS. The chemical composition of regions 1–4 are listed in Table 1.

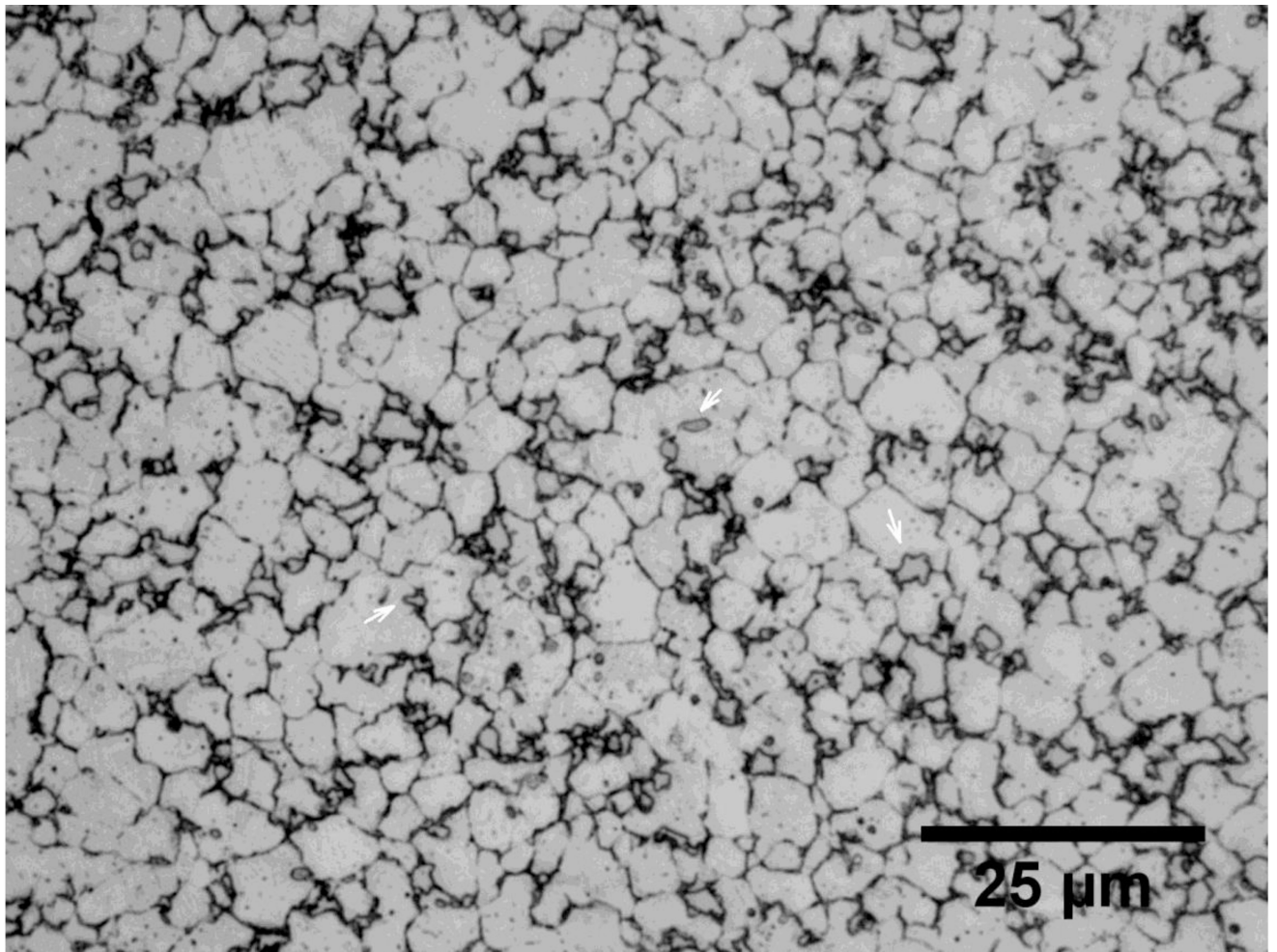


Figure 7. Optical micrograph showing grain size refined to a few microns in the wrought alloy. Carbides of 0.5–1 μm (as arrowed in the micrograph) were uniformly distributed in the matrix.

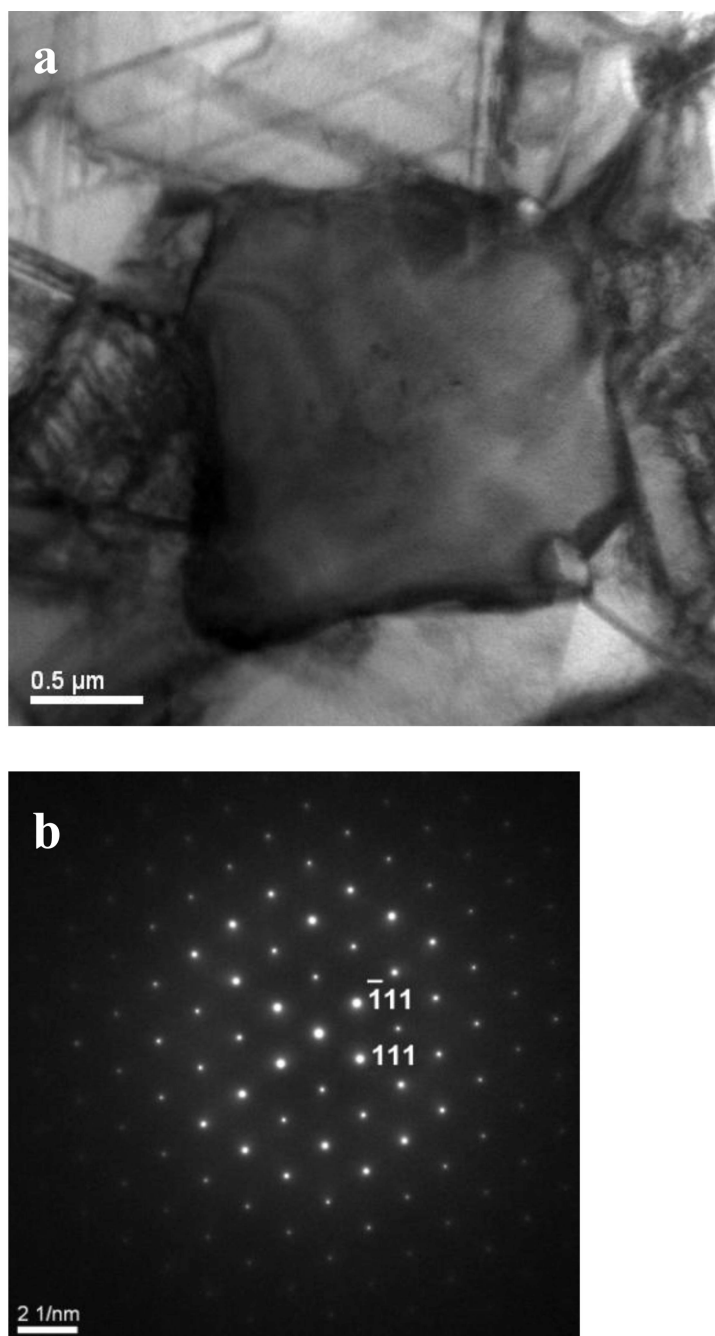


Figure 8.
(a) Bright-field TEM micrograph of a carbide in the wrought alloy. (b) Electron diffraction pattern along the $[01\bar{1}]$ zone axis.

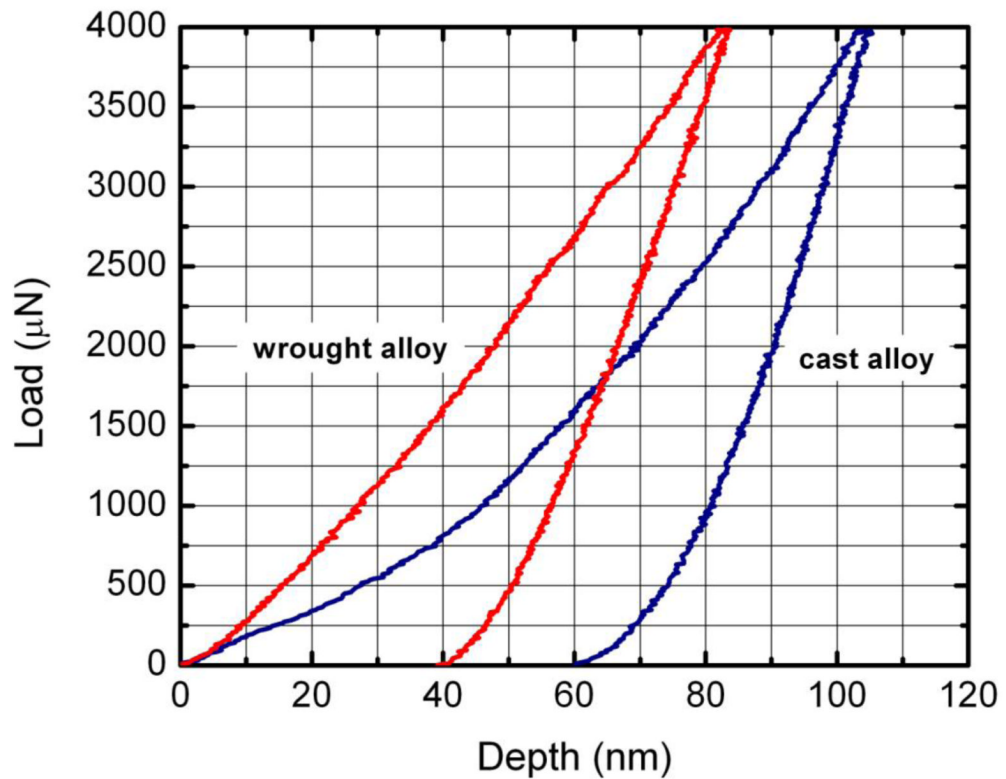
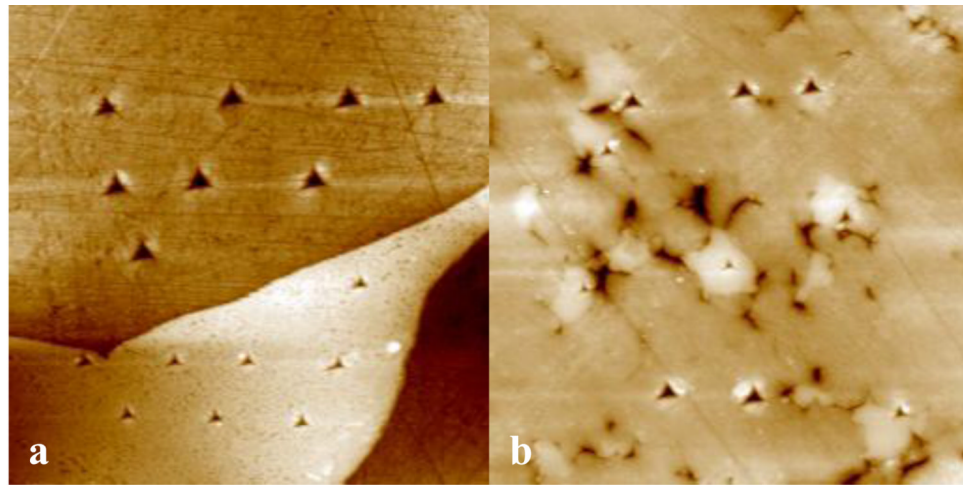


Figure 9.

AFM image of indents in the (a) cast alloy and (b) wrought alloy. The scanning areas were $20\ \mu\text{m} \times 20\ \mu\text{m}$. The indentation size in cast alloy is greater than that in wrought alloy. The corresponding force-displacement curves are showed in (c). The wrought alloy carbide underwent less plastic deformation.

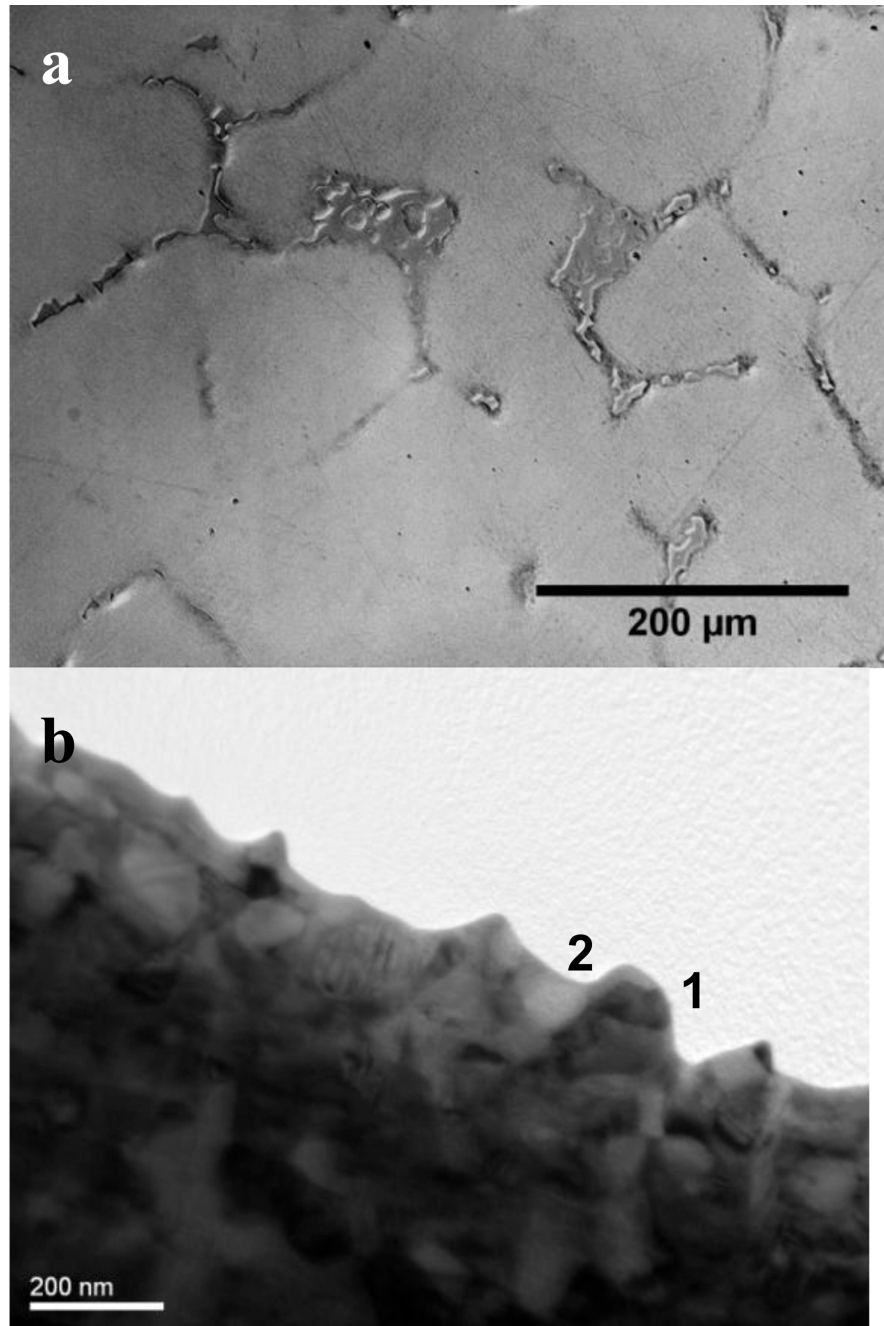


Figure 10.

(a) Optical and (b) TEM micrographs of the specimen cooled at 0.2 °C/s. The hard phases are composed of ~100 nm fine structures.

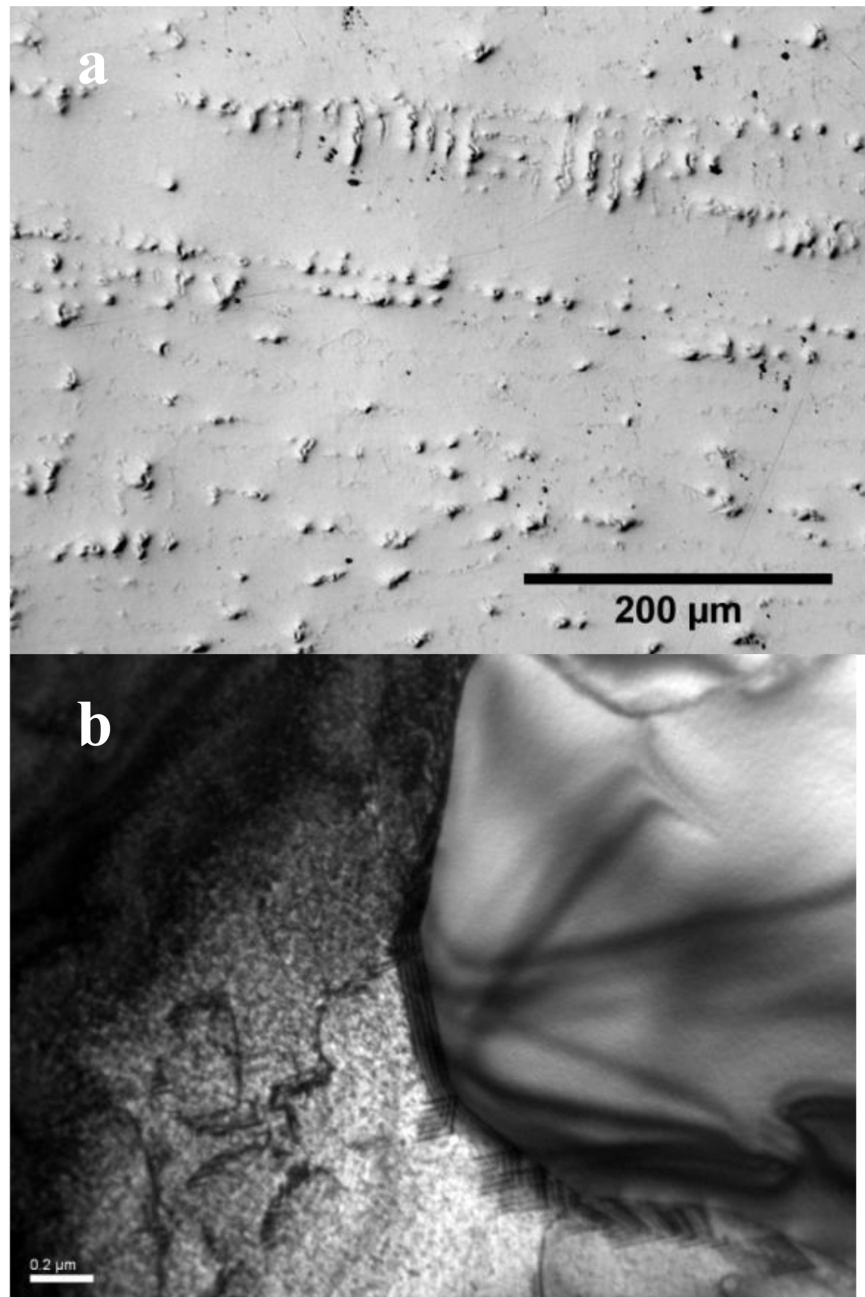


Figure 11.

(a) Optical micrograph of the specimen cooled at 50 $^{\circ}\text{C/s}$. The hard phases are 5–10 μm large. (b) TEM micrograph showing that the hard phase is single phase carbide.

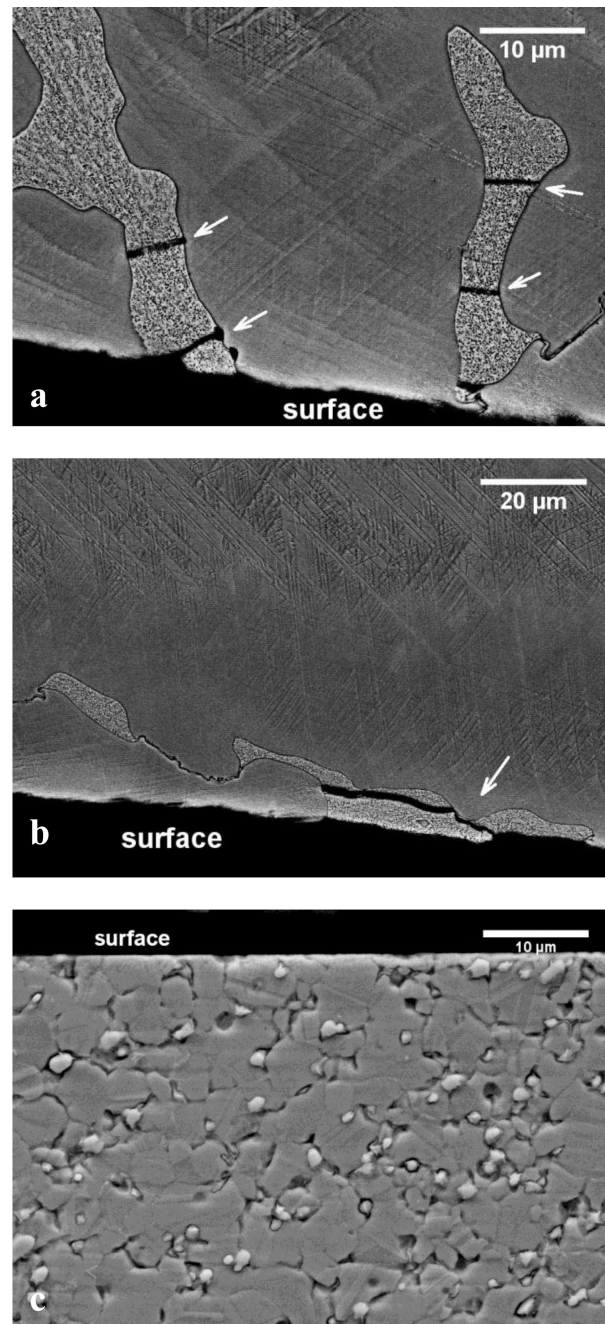


Figure 12.

(a) and (b) Cross-section SEM micrographs of a retrieved implant (head component) made of cast alloy. Fractures of the mixed hard phases near the surface frequently occurred as arrowed in the images. (c) The single phase carbides in a wrought alloy were intact after 5 million cycles simulator test.

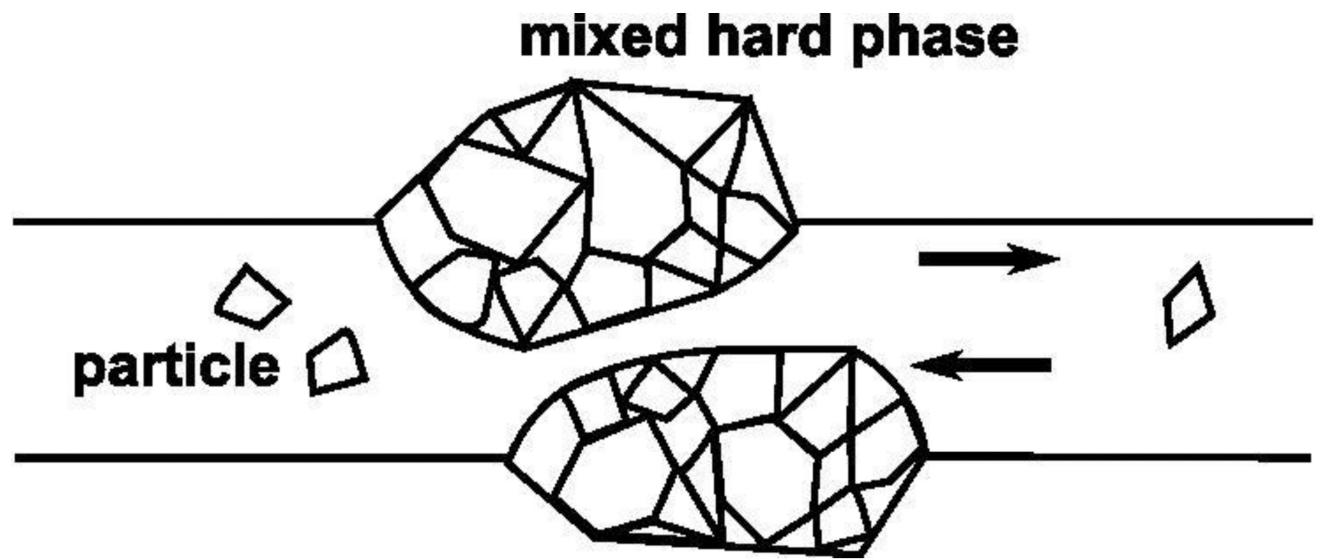


Figure 13.
Schematic of nanoparticles generated from mixed hard phases during wear.

Table 1

Chemical composition of the four regions marked in Figure 6. The standard deviation is listed.

Wt.%	Cr	Co	Mo
<i>1</i>	57.14 (0.54)	28.62 (0.48)	14.24 (0.77)
<i>2</i>	62.57 (0.59)	30.53 (0.53)	6.90 (0.59)
<i>3</i>	22.11 (0.38)	75.05 (0.79)	2.85 (0.45)
<i>4</i>	22.27 (0.54)	43.74 (0.85)	33.99 (1.65)

Table 2

Chemical compositions of the hard phases and matrices cooled at different rates.

Wt.%		Cr	Co	Mo
cooled at 0.2 °C/s (Figure 10b)	nanophase 1	56.55 (1.34)	18.54 (0.76)	24.91 (1.59)
	nanophase 2	20.51 (0.75)	27.27 (0.92)	52.22 (1.30)
	matrix	24.02 (0.81)	68.33 (1.24)	7.66 (1.35)
cooled at 50 °C/s	single phase carbide	32.07 (0.56)	44.77 (0.68)	23.16 (0.90)
	matrix	64.74 (0.44)	28.39 (0.33)	6.87 (0.47)

Table 3

Nano-hardness of the phases of CoCrMo alloys (unit: GPa). The numbers of measurement are shown in the brackets.

	hard phase	matrix
cooled at 0.2 °C/s	15.0 ± 2.2 (34)	6.1 ± 0.3 (22)
cooled at 50 °C/s	16.3 ± 0.9 (8)	6.2 ± 0.3 (31)
the retrieval made of cast alloy	15.7 ± 9 (7)	6.4 ± 3 (8)
wrought	30.7 ± 2.6 (7)	9.4 ± 0.8 (11)