



On the cementite behavior during tribology and experimental methods of microscale wear

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Symbols

A_I	Indentation contact area
A_P	Scratch contact area projected in the lateral direction
A_S	Scratch contact area projected on the sample surface
A _{S,Hertz}	Hertzian solution for the scratch contact area
α	Half-angle of the conical part of the tip
β	Dimensionless parameter for nanoindentation
d init	Distance of the maximum penetration depth
Ε	Elastic modulus
E _{eff}	Effective elastic modulus
E _{sample}	Elastic modulus of the sample
E_{tip}	Elastic modulus of the tip
Е	Geometrical constant for nanoindentation
ε _e	Parameter for the magnitude of the elastic recovery
F	Area function for nanoindentation
F_N	Normal force
F _{N,max}	Maximum normal force
F_T	Tangential force
Н	Indentation hardness at a particular penetration depth
H_I	Indentation hardness
H_P	Plowing hardness
H_S	Scratch hardness
<i>H</i> _{<i>S</i>,0}	Macroscopic scratch hardness
Hv	Vickers hardness

H_0	Macroscopic indentation hardness
h	Penetration depth
h_{avg}	Average penetration depth in the steady-state wear region
h_c	Contact depth
h _{ind}	Penetration depth during indentation
h _{init}	Mamimum penetration depth during transition to wear
h_t	Transition depth between spherical and conical indentation
h^*	Characteristic depth
$m_1 m_8$	Area function constants
v_{sample}	Poisson ratio of the sample
$ u_{tip}$	Poisson ratio of the tip
R	Radius of the spherical part of the tip
S	Contact stiffness
σ_y	Yield strength
V _{pile-up}	Pile-up volume
w	Wear track width
W _{max.slope}	Wear track width between the locations of the maximum slope
$W_{pile-up}$	Wear track width between the highest points of the side pile-ups
Wsurface	Wear track width at the undeformed surface height

Abbreviations

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
APT	Atom probe tomography
BF	Bright-field imaging mode
CSM	Continuous stiffness measurement
DF	Dark-field imaging mode
DFT	Density functional theory
EBSD	Electron backscatter diffraction
EDS	Energy-dispersive X-ray spectroscopy
FIB	Focused ion beam
NR	Nanocrystalline region
SAA	Selected area aperture
SAED	Selected area electron diffraction
SAM	Scanning Auger microprobe
SD	Sliding direction
SLG	Soda-lime glass
SEM	Scanning electron microscope
STEM	Scanning transmission electron microscope
TEM	Transmission electron microscope
TR	Transition region
UFGR	Ultra-fine-grained region
WEL	White etching layer
WEA	White etching area
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract

During contact, the tribological behavior of steels largely depends on the wear response of the individual phases, which include the matrix phase, e.g., ferrite, martensite, and the strengthening phase, i.e., cementite. The morphology, fraction, and interplay between cementite precipitates and the matrix affect the tribological response of steel in different ways. However, the present understanding of the mechanisms influencing the tribological behavior of cementite-strengthened steels is limited. This limitation is because cementite is conventionally embedded in the matrix, and it is difficult to isolate its wear behavior from the matrix influence. For the development of wear-resistant materials, the microscale wear experiment has recently gained popularity since it allows to assess micro-and nanoscale deformation mechanisms during controlled sliding under a low normal force. This technique has several advantages when compared to the conventionally employed nanoindentation but requires a unified protocol for the quantitative measurement of the wear resistance and established relations to indentation. The first objective of this thesis is to characterize bulk polycrystalline cementite deformation, microstructure, and chemical evolution during single-pass and multi-pass wear. The second objective is to investigate the relations between indentation and single-pass wear experiment, analyze the available models for scratch hardness, and examine their advantages and disadvantages.

The bulk polycrystalline cementite (~95 wt.% Fe₃C) sample was fabricated by spark plasma sintering and contains minor fractions of ferrite, graphite, and wüstite. The sample was subjected to the microscale single-pass wear at 31 GPa reference Hertzian pressure and to the macroscale multi-pass wear at 3.3 GPa. The initial characterization demonstrated the presence of the slip traces, ductile abraded particles, and pile-up. The slip traces analyzed by electron-backscattered diffraction (EBSD) correspond to the dislocation activity on the (001), (010), (101), (110), and (011) planes. The (scanning) transmission electron microscopy ((S)TEM) analysis of the wear tracks cross-sections reveals three deformed layers below the contact surface. In the outermost nanocrystalline layer, the dominating deformation mechanisms are grain boundary sliding and grain rotation. The deformed middle layer contains fragmented grains that undergo dislocation slip and grain boundary sliding. In the bottom layer, grains deform by slip and occasionally shear bands. The cross-sections from single-pass and multi-pass wear tracks differ mainly by the thickness of the deformed layers. The strengthening of the microstructure deformed by the multi-pass wear increases the local nanoindentation hardness by up to 2.7 GPa.

The diffraction pattern analysis and the dark-field imaging reveal the formation of carbonrich Hägg carbide (Fe_5C_2) nanocrystallites due to the severe shear deformation in the uppermost layer. Based on atom probe tomography (APT) studies, the nanocrystalline layer contains higher carbon and oxygen fractions than the undeformed cementite. It was concluded that the two primary potential sources of excess carbon are the tribooxidation of cementite and deformation-induced dissolution of the present homogeneously distributed graphite particles. According to the electron dispersive X-ray spectroscopy (EDS), shear deformation in the outermost deformed layer resulted in partial decomposition and mechanical mixing of the non-cementite inclusions and partial elemental homogenization. The X-ray photoelectron spectra (XPS) obtained from the single-pass wear track array and undeformed region demonstrated similar elemental depth profiles. Comparing the ratios between carbon and iron compounds confirmed that partial decomposition of graphite particles provides the driving force for Hägg carbide formation by uptake of the released carbon by Fe₃C.

To analyze the scratch hardness models and examine the links between indentation and wear, single-pass experiments were conducted on aluminum, copper, austenitic steel, cementite, soda-lime-glass, and silicon. The main mechanisms determining the penetration depth increase and wear track groove evolution during the transition from indentation to wear are contact area conservation, elastic recovery, and the front pile-up formation. The measurements of the wear track grooves in [111] and [001] austenitic steel grains by confocal microscope show the minor influence of the crystallographic orientation during the initial depth increase and a strong effect during the subsequent depth decrease. This influence is pronounced through the greater pile-up volume in the [001] grain. The scratch hardness values were calculated using four contact area models employing contact depth and three width definitions. For the depth-based contact area, the scratch hardness has fewer sources of experimental errors and leads to monotonic trends for all studied materials. The comparison of the scratch hardness trends elucidated the presence of scratch size effect, inverse scratch size effect, and tip size effect. It was confirmed that scratch and nanoindentation hardness are not equal and that scratch hardness provides a higher value than nanoindentation hardness. The ratios between nanoindentation and scratch hardness reach nearly constant values at the highest normal forces applied (0.28-0.38 for copper, 0.47-0.61 for aluminum). It was also demonstrated that the Hertzian elastic solution as a first approximation for scratch contact area provided a good estimation at the lower normal force range for soda-lime glass, cementite, and silicon. The Hertzian elastic solution can also be applied as the lower boundary for the scratch contact areas for all materials.

Zusammenfassung

Während des Kontakts hängt das tribologische Verhalten von Stählen wesentlich von dem Verschleißverhalten der einzelnen Phasen ab, zu denen die Matrixphase, z.B. Ferrit, Martensit, und die Verfestigungsphase, d.h. Zementit, gehören. Die Morphologie, der Anteil und das Zusammenspiel von Zementit-Ausscheidungen und der Matrix beeinflussen das tribologische Verhalten von Stählen auf unterschiedliche Weise. Jedoch ist das aktuelle Verständnis der Mechanismen, die das tribologische Verhalten von Zementit verfestigten Stählen beeinflussen, begrenzt, weil der Zementit konventionell in der Matrix eingebettet ist und es daher schwierig ist, sein Verschleißverhalten von dem Matrixeinfluss zu isolieren. Bei der Entwicklung von verschleißfesten Werkstoffen hat das mikroskopische Verschleißexperiment in letzter Zeit zunehmend an Popularität gewonnen, da es die Untersuchung von mikround nanoskopischen Verformungs¬mechanismen während des kontrollierten Gleitens unter einer kleinen Normalkraft ermöglicht. Dieses Verfahren hat mehrere Vorteile im Vergleich zur konventionellen Nanoindentation, benötigt aber ein einheitliches Protokoll für die quantitative Messung der Verschleißfestigkeit und für die Bestimmung der Zusammenhänge zur Indentation. Das erste Ziel dieser Doktorarbeit ist die Beschreibung der Verformung des polykristallinen Zementits, seiner Mikrostruktur und seiner chemischen Veränderungen während des ein- und mehrmaligen Verschleißes. Das zweite Ziel ist die Erforschung der Zusammenhänge zwischen der Indentation und dem einmaligen Verschleißexperiment, die Analyse der verfügbaren Ritzhärtemodelle und die Untersuchung ihrer Vor- und Nachteile.

Eine polykristalline Zementitprobe (~95 Gew.-% Fe₃C) wurde durch Spark-Plasma-Sintern hergestellt und enthält geringe Anteile von Ferrit, Graphit und Wüstit. Die Probe wurde dem mikroskopischen einmaligen Verschleiß bei einem Hertzschen Referenzdruck von 31 GPa und dem makroskopischen mehrmaligen Verschleiß bei 3.3 GPa ausgesetzt. Die Analyse zeigte das Auftreten von Gleitspuren, duktilen Abriebpartikeln und Anhäufungen. Die mittels Elektronenrückstreubeugung (EBSD) analysierten Gleitspuren entsprechen der Versetzungsaktivität auf den (001)-, (010)-, (101)-, (110)- und (011)-Ebenen. Die (rastergestützte) Transmissionselektronenmikroskopie ((S)TEM)-Analyse der Verschlei߬spurguerschnitte zeigt drei Verformungsschichten unter der Kontaktfläche. In der äußersten nanokristallinen Schicht sind die dominierenden Verformungsmechanismen das Korngrenzengleiten und die Kornrotation. Die mittlere Verformungsschicht enthält fragmentierte Körner, die Versetzungsgleiten und Korngrenzengleiten aufweisen. In der unteren Schicht verformen sich die Körner durch Versetzungsgleiten und vereinzelt durch

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Scherfugen. Die Querschnitte von ein- und mehrfachen Verschleißspuren unterscheiden sich hauptsächlich durch die Breite der verformten Schichten. Die Verfestigung der durch den Mehrfachverschleiß verformten Mikrostruktur erhöht die lokale Nanoindentationshärte um bis zu 2.7 GPa.

Die Beugungsmusteranalyse und die Dunkelfeldaufnahme zeigen die Bildung von kohlenstoffreichen Hägg-Karbid (Fe₅C₂)-Nanokristalliten aufgrund der starken Scherverformung in der obersten Schicht. Die Atomsondentomographie (APT) zeigt, dass die nanokristalline Schicht höhere Kohlenstoff- und Sauerstoffanteile enthält als der unverformte Zementit. Daraus wurde schlussgefolgert, dass es potenziell zwei Primärquellen für den überschüssigen Kohlenstoff gibt: die Tribooxidation von Zementit und die verformungsbedingte Zerlegung der vorhandenen homogen verteilten Graphitpartikel. Die elektronendispersive Röntgenspektroskopie (EDS) zufolge führt die Scherverformung in der äußersten verformten Schicht zu einer teilweisen Zersetzung und mechanischen Vermischung der Nicht-Zementit-Einschlüsse sowie zu einer teilweisen Homogenisierung der Elementzusammensetzung. Die Röntgen-Photoelektronenspektren (XPS), die von einem Feld aus einzelnen Verschleißspuren und dem Referenzgebiet bestimmt wurden, ergaben ähnliche Elementtiefenprofile. Deswegen, bestätigte der Verhältnisvergleich zwischen Kohlenstoff- und Eisenkomponenten, dass die partielle Zerlegung von Graphitpartikeln die treibende Kraft für die Bildung von Hägg-Karbid ist, durch die der freigesetzte Kohlenstoff von Fe₃C aufgenommen wird.

Für die Analyse der Ritzhärtemodelle und die Untersuchung der Zusammenhänge zwischen Indentation und Verschleiß wurden Einweg-Verschleißversuche an Aluminium, Kupfer, austenitischem Stahl, Zementit, Kalk-Natron-Glas und Silizium durchgeführt. Die Hauptmechanismen, die für die Zunahme der Eindringtiefe und die Entwicklung der Verschleißspuren beim Übergang von der Indentation zum Verschleiß verantwortlich sind, sind die Kontaktflächenerhaltung, die elastische Entlastung und die Bildung der vorderen Anhäufung. Die Messungen der Verschleißspuren in [111] und [001] Körnern von austenitischem Stahl mit dem konfokalen Mikroskop zeigen den geringen Einfluss der Kristallorientierung während der ursprünglichen Tiefenerhöhung und einen starken Einfluss während der folgenden Tiefenabnahme. Dieser Orientierungseinfluss ist durch das größere Anhäufungsvolumen im [001]-Korn deutlich ausgeprägt. Die Werte der Ritzhärte wurden anhand von vier Kontaktflächen-Modellen berechnet, die die Kontakttläche weist die Ritzhärte weniger experimentelle Fehlerquellen auf und führt bei allen untersuchten Materialien zu monotonen Trends. Der Vergleich der Ritzhärte-Trends

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verdeutlichte das Vorhandensein von Größeneffekt beim Verschleiß: inversem Ritzgrößeneffekt und Spitzengrößeneffekt. Es wurde bestätigt, dass die Ritz- und Nanoindentationshärte nicht gleich sind und dass die Ritzhärte einen höheren Wert als die Nanoindentationshärte hat. Die Verhältnisse zwischen Nanoindentations- und Ritzhärte erreichen bei den höchsten angewandten Normalkräften nahezu konstante Werte (0.28-0.38 für Kupfer, 0.47-0.61 für Aluminium). Es wurde auch gezeigt, dass die elastische Hertzsche Lösung als erste Approximation für die Ritzkontaktfläche eine gute Abschätzung im unteren Normalkraftbereich für Kalk-Natron-Glas, Zementit und Silizium liefert. Die Hertzsche Lösung ist auch die untere Grenze für die Ritzkontaktflächen für alle Materialien.

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1. Introduction

1.1 Motivation

The importance of controlling the wear behavior of materials became evident since the development of the first machines designed to experience sliding and rolling contacts [1–4]. A 2017 review by Holmberg and Erdemir [5] shows that about 23% of the world's energy resources are spent on overcoming friction (20%) and wear (3%). Although the wear-related dissipation is a relatively small fraction of all energy losses, those losses are claimed to be more critical because replacement of the engineering components damaged by wear and wear failures cause massive operational disruptions and high costs [5]. The present global objective for more rational consumption of energy resources and reduction of CO_2 emissions further emphasizes the significance of the development of wear-resistant materials.

According to the classification of wear forms, abrasive wear has a great relative importance in engineering applications and is encountered in 36-58% of reported cases [6,7]. For many engineering applications that require high abrasive wear resistance, e.g., rails [8–11], wheels [12–14], bearings [15,16], and concrete-mixing drums [17], steels that contain cementite are employed. On the one hand, cementite precipitates assist in strengthening and strain hardening [18–22], increasing steel hardness, and reducing wear loss [23,24]. On the other hand, cementite also can contribute to rapid erosion through precipitate fracture [25–27] or the microstructure transformation into the brittle nanocrystalline subgrain structure [8,9,16,28]. Therefore, the deformation behavior of cementite has to be elucidated for the development or tailoring of wear-resistance steels.

The effect of cementite precipitates on the wear resistance of steels relies on multiple factors, such as cementite morphology and loading conditions. One of the challenges that arise when studying cementite's wear behavior is related to its presence as a precipitate in a matrix (e.g., ferrite, martensite). Since the microstructure and chemical evolution during wear are partially determined by the cementite interaction with the surrounding matrix in the multiphase steels, the individual mechanisms in cementite are difficult to isolate. The recent development of bulk cementite fabrication via spark plasma sintering made it possible to exclude the influence of matrix and the cementite-matrix interactions [29]. The present research on the bulk polycrystalline cementite behavior during tribology was carried out based on the macroscale wear experiments [30,31]. Nonetheless, the

activated micro- and nanoscale deformation mechanisms and potential changes in chemical composition during wear in cementite were not explored.

The loading conditions of engineering components that employ cementite-strengthened steels are rolling-sliding contacts under various dynamic loads and velocities. The contacts occur at numerous asperities due to the incipient roughness of the surfaces. For the systematic, controlled wear behavior investigations, the contacts are often reproduced on the micro- and nano-scale, i.e., single asperity contacts [32-34]. To properly assess the wear performance of the studied material, the wear experiment needs to be wellestablished: the deformation mechanisms have to be well understood, and the experiment should provide a unified quantitative measure of the wear resistance. In this regard, the following challenges exist. Firstly, the mechanisms of the wear track groove formation during the transition from the quasi-static indentation to the steady-state dynamic wear are not entirely described [35-37]. Secondly, the scratch hardness analysis often involves competing measurement protocols that affect the results and thus cannot be effectively used to compare the wear resistance between different scientific studies. Thirdly, while nanoindentation is conventionally employed to access the near-surface mechanical properties, e.g., nanoindentation hardness [38], its relationship to the wear test and scratch hardness, better suited for the wear resistance analysis, is not explicitly determined [35,39-43].

To conclude, the development of wear-resistant steel involves several obstacles. These include the lack of understanding of the polycrystalline cementite wear behavior, as well as the questions related to the wear experiment during the transition stage, wear resistance quantification, and relations to nanoindentation. In this thesis, we focused on clarifying these aspects using the single- and multi-pass wear experiments.

1.2 Objectives and investigation approaches

As can be concluded from the previous section, the work in this thesis can be divided into two parts. In the first part, a bulk cementite sample produced by spark plasma sintering was chosen to analyze the cementite wear behavior. We compare the deformed microstructures under different tribological loading conditions by carrying out both singlepass and reciprocal multi-pass tests. During wear tests, high contact pressures had to be reached to produce severe plastic deformation inside the wear track. We aimed to reveal the micro- and nanoscale deformation mechanisms activated in cementite during these loading scenarios using a number of characterization techniques. The observation of undeformed and deformed surfaces was performed using a scanning electron microscope (SEM). The deformation behavior of cementite was studied by electron backscatter diffraction (EBSD) for a slip trace analysis as well as transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) using the specimens extracted via focused ion beam (FIB) milling to analyse the microstructure evolution. Using nanoindentation, we determine the effect of the multi-pass wear on the near-surface hardness of cementite. X-ray diffraction (XRD) was used to conduct grain size and phase analysis both in undeformed and deformed regions. The chemical evolution of cementite due to the deformation is assessed via atom probe tomography (APT), energy-dispersive X-ray spectroscopy (EDS) in STEM, Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS).

By using the abovementioned approaches, we seek the answers to the following questions:

- What are the dominant deformation mechanisms in cementite during sliding wear?
- How does the activation of deformation mechanisms in cementite depend on the shear stress intensity and grain size?
- What effect do the tribological loading and the associated deformation have on the elemental and phase composition and their distribution?

The second part of this thesis is dedicated to the single-pass wear test as a measurement technique. We examine the wear track groove during the transition from indentation to steady-state wear, the effect of the applied scratch contact area model on the scratch hardness, and the potential relations between nanoindentation and scratch hardness. It is thus essential to perform experiments on the materials with varying mechanical properties (aluminum, copper, austenitic stainless steel, cementite, soda-lime glass, and silicon) to identify the trends that are not material-related. Moreover, we use two indenter tips of different radii to account for the tip size effect and conduct tests in a large force range to study normal force dependencies. The geometrical parameters of the wear track groove are recorded during the experiment by the indenter tip and post-deformation via a confocal microscope.

By using this strategy, we aim to answer the following questions:

- What mechanisms govern the penetration depth and wear track groove formation during the transition from indentation to wear for different materials?
- How does the measured scratch hardness depend on the applied scratch contact area models, and what is the most reliable way to determine it?
- Which correlations exist between the scratch hardness and nanoindentation hardness for different material classes?

1.3 Thesis structure

The scientific background on cementite properties and applications, nanoindentation, and wear experiments is encompassed in Chapter 2. Chapter 3 describes the details of experimental procedures and characterization techniques. In following Chapter 4, the results demonstrate the dominating deformation mechanisms in cementite during single-pass and multi-pass wear experiments. In addition, the same chapter presents the change in the subsurface hardness due to the multi-pass sliding and the initial indications of the phase transformation below the contact surface. Chapter 5 concentrates on the chemical composition changes during single-pass wear in cementite and studies the phase transformation below the contact surface in more detail. Chapter 6 discusses the transition from static indentation to dynamic wear, i.e., the evolution from stationary to sliding contact. In Chapter 7, the focus lies on the scratch hardness evaluation methods, secondary influences that affect the scratch hardness, and the relation between nanoindentation and scratch hardness. In Chapters 6 and 7, the studies were done on the larger materials sets, including soft and ductile as well as hard and brittle materials. The final Chapter 8 summarizes the findings of this thesis and provides the conclusion.

2. Background

2.1 Cementite in steels for tribological applications

2.1.1 Cementite structure, hardness, and stability

Cementite is an iron carbide with a composition of Fe₃C, commonly found in steel and cast-iron alloys. According to the Fe-C binary phase diagram, cementite contains 6.67 wt.% carbon [44]. The unit cell of cementite is orthorhombic, primitive (space group Pnma), and relatively large with lattice parameters a = 0.50837 nm, b = 0.67475 nm, and c = 0.45165 nm. It contains 12 iron and 4 carbon atoms in prismatic interstitial sites (Fig. 2.1). The smaller octahedral interstitial sites generally remain empty unless the carbon content exceeds the stoichiometric 25 at.% [45,46]. The chemical bonding in cementite was confirmed to be a complex mixture of metallic, covalent, and ionic bonding [47,48].



Fig. 2.1. The cementite unit cell with 12 iron atoms (blue spheres) and 4 carbon atoms (red spheres).

The deformability of cementite is partially governed by its crystal structure. The crystal structure's anisotropy is reflected in the anisotropy of the cementite properties, e.g., elastic constants [47,49,50]. Based on the density functional theory (DFT) simulations of the ideal tensile and shear strength as well as nanoindentation studies, some degree of plastic

anisotropy in cementite was demonstrated [48,50,51]. Due to the relatively large and primitive unit cell, dislocations in cementite have large Burgers vectors, i.e., magnitude equivalent to the lattice parameters or larger [52,53]. As a consequence, dislocation movement is rather difficult, and the number of independent slip systems available for the accommodation of plastic deformation is limited [45,54–56]. The experimentally observed slip systems are (100)[010], (100)[001], (001)[100], (001)[010], (010)[001] and (010)[100] [50,52,55]. The (011), (110), and (101) planes are more likely to be activated at high temperatures, specific cementite morphologies, or high strains [53,55,57–59]. Karkina et al. [60] demonstrated that for cementite-ferrite steels, only 6 out of 12 ferrite slip systems $1/2 < 111 > \{110\}_F$, and only 3 out of $12 1/2 < 111 > \{110\}_F$ slip systems are available for the slip transfer across the ferrite-cementite interface. Therefore, brittle fracture is often preferable to dislocation-mediated plasticity, and cementite is generally considered a hard and inherently brittle constituent.



Fig. 2.2. Deformability of the cementite lamellae in pearlite as a function of lamellae size and interlamellar spacing for different loading conditions [22].

Nonetheless, cementite tends to exhibit plasticity in cases of specific microstructure morphologies and loading conditions [22,61]. In one of the earlier studies by Langford [22] (Fig. 2.2), the deformation nature of lamellar cementite, according to other research works, was classified according to the lamellae thickness, interlamellar spacing, and loading conditions. Based on the combined evidence, a size effect on the deformability of cementite lamellae was concluded: no evidence of plasticity was found of >0.1 μ m thick lamellae as well as no evidence for brittleness of the <0.01 μ m thick lamellae [22]. In

addition, the role of the loading conditions was emphasized since lamellae tend to fracture due to tension and deform plastically by wire drawing.

The recent investigations of steel deformation by tribological loading also demonstrate plasticity of cementite precipitates, both of lamellar and spheroidal shape. Todaka et al. [62] reported both brittle fracture and coarse slip steps from dislocation slip of lamellar cementite in the steel with an initial interlamellar spacing of 890 nm deformed by cold rolling to the final reduction of 30-60 %. The same cold rolling experiments were carried out on the pearlitic steels with interlamellar spacings of 710 nm and 114 nm in the work of Umemoto et al. [63]. The typical morphologies of deformed cementite after cold rolling are demonstrated in Fig. 2.3. In the finer pearlite (114 nm), the authors more often observed homogeneous lamella thinning by slip when the activated slip system in ferrite and the lamella plane are almost parallel. In the coarser pearlite (710 nm), inhomogeneous slip leads to the coarse slip step formation up to the lamellae fragmentation into 200-300 nm thick blocks that afterwards slide past one another. Some fracture of cementite lamellae in coarser cementite was found as well (Fig 2.3).





The dominance of grain boundary sliding over dislocation slip at sufficiently small grain sizes was also observed in molecular dynamics simulations of nanocrystalline cementite under uniaxial tensile loading at a high strain rate by Ghaffarian et al. [56]. Zhang et al.

[58] analyzed martensitic bearing steel with embedded spheroidized cementite after a surface mechanical rolling treatment. Direct slip transfer from the matrix into the precipitate was not observed. However, the inhomogeneous plastic flow of the surrounding martensite and the strain incompatibilities result in local stress concentrations. These stress concentrations allow for dislocation nucleation at these sites. Similar observations were made also for high pressure torsion experiments [15].

Due to its exceptional hardness, cementite is often used as a strengthening constituent in bearing, rail, and wheel steels. However, the hardness measurement of pure cementite is complicated because pure cementite is difficult to fabricate. Several experimental studies measured the hardness of pure cementite prepared using physical vapor deposition or spark plasma sintering. For the 2.5 μ m thick cementite film samples prepared by physical vapor deposition with a grain size of about 50 nm, the Vickers microhardness H_V at room temperature was determined as 1230-1260 HV, equivalent to 12.1-12.4 GPa [64]. The samples prepared by spark plasma sintering have a larger grain size and contain porosity which reduces the measured hardness. For the sintered cementite sample, the room temperature Vickers microhardness equals 9.1-10.8 GPa [30,31,65] (Fig. 2.4). These results are consistent with the 9.8 GPa Vickers microhardness recorded for 30-60 μ m cementite plates inside the steel sample [66].



Fig. 2.4. (a) An example of a Vickers indentation impression in a sintered bulk cementite sample with the addition of manganese ($Fe_{0.8}Mn_{0.2}$)₃C). (b) Vickers hardness-temperature dependence of sintered bulk cementite ($Fe_{3}C$). Adapted from [65].

Cementite is a metastable compound with respect to the α -iron (ferrite) and graphite below the eutectoid temperature in the Fe-C phase diagram [67,68]. If cementite, ferrite, and

graphite exist together, ferrite and graphite form a stable equilibrium mixture. If only graphite is present with cementite, cementite remains stable and does not decompose. [45,69,70]. Alloying with certain substitutional solute elements, such as manganese or chromium, is beneficial for its thermodynamic stability [71,72]. Such elements reduce the rate at which cementite decomposes into graphite and allow for the production of bulk cementite samples with low porosity volume [63,72].

Among known iron carbides (Fe₇C₃, ϵ -Fe_{2.4}C, η -Fe₂C, χ -Fe₅C₂, θ -Fe₃C), cementite has the lowest carbon fraction and is the most stable phase. As a consequence, during the tempering of the carbon-rich martensite, the experimentally observed transformation sequence is the following [73]:

Martensite $\rightarrow \epsilon$ -carbide (Fe_{2.4}C) + α -iron $\rightarrow \eta$ -carbide (Fe₂C) + α -iron $\rightarrow \gamma$ -carbide (Fe₅C₂) + α -iron $\rightarrow \theta$ -carbide (Fe₃C) + α -iron.

Thermal treatment eventually leads to the replacement of the initial martensite and all carbon-rich carbides with cementite and ferrite. Moreover, cementite is the only carbide that precipitates when the carbon concentration is relatively small. Nonetheless, other iron carbides tend to form if the driving force (excess carbon fraction) is sufficiently large [74]. For example, monoclinic Hägg carbide (Fe_5C_2) is the most stable transition carbide before the stable mixture of iron and cementite forms during high-carbon martensite tempering [73]. Hägg carbide precipitates can either coexist with cementite or grow at the cost of cementite at sufficiently high carbon concentrations, e.g., interpenetrating microsyntactic intergrowth layers or planar defects [46,74–78].

2.1.2. Wear behavior of steels containing cementite

Steels for tribological applications have different microstructures to resist wear under specific loading conditions, i.e., cyclic rolling-sliding contacts under varying forces and velocities. In multiphase steel microstructures, the interactions between cementite precipitates and the matrix phase partially define the deformation behavior [15,63,79]. Cyclic tribological loading causes continuous microstructural changes below the contact surface that, in return, constantly influence the frictional response [80]. As a consequence, when steel is exposed to a tribological load, there is a continuous interplay between altering cementite morphology, change of the dominant deformation mechanisms, and the effect cementite imposes on the overall wear performance.

Depending on the steel production procedure, cementite precipitates have different morphology and are embedded in the matrix of ferrite or martensite. Fig. 2.5 demonstrates possible morphologies for the AISI 52100 high-carbon steel conventionally used for the production of bearings [58,81,82].



Fig. 2.5. Microstructures and different cementite morphologies in AISI 52100 steel obtained by specific production methods and thermal treatments: (a) pearlite (lamellar cementite in a ferrite matrix), (b) spheroidite (spheroidized cementite in a ferrite matrix), (c) tempered martensite (spheroidized cementite in martensite matrix), (d) lower bainite (fine needle-like cementite particles in ferrite plates). Adapted from [58,81,82].

In hot-rolled pearlitic steel (Fig. 2.5a), the cooperative formation of cementite and ferrite results in the growth of so-called colonies. The colonies resemble stacks of alternating ferrite and cementite lamellae. In steels with a high fraction of carbon, proeutectoid cementite also precipitates at the prior grain boundaries of the initial austenite. After the spheroidization annealing, pearlitic microstructure transforms into equiaxed spherical cementite particles embedded in the ferritic matrix (spheriodite, Fig. 2.5b). The

microstructure of spheroidized cementite in the martensite matrix (tempered martensite, Fig. 2.5c) is achieved by quenching and subsequent tempering of the austenized steel. The lower bainite microstructure (Fig. 2.5d) is obtained by the isothermal transformation in the temperature range that is lower than that required for the production of pearlite. Cementite in lower bainite is present as very fine (few nm thick) needle-like particles inside the large ferrite plates.

The relations between steel microstructures and tribological response have been thoroughly examined. In the study by Ueda et al. [23], the wear performances of four steels with different microstructures and cementite morphologies were compared during a two-cylinder rolling contact wear experiment (Fig. 2.6a). The authors analyzed the weight loss of eutectoid pearlite (pearlitic steel in Fig. 2.6a), hypereutectoid pearlitic steel (cementite steel in Fig. 2.6a), spheroidized cementite in the martensite matrix (tempered martensite steel in Fig. 2.6a), as well as spheroidized cementite in the ferrite matrix (spheroidal carbide steel in Fig. 2.6a). The results emphasize the strong effect of the interactions between cementite precipitates and the matrix on the wear behavior of steels.

Although all examined steels had a similar Vickers hardness H_v , the lowest weight loss was observed in the case of the eutectoid pearlitic steel (Fig. 2.6a). Pearlite generally has better tribological stability than martensite, bainite, and ferrite with spheroidized cementite [23,83–85]. Cementite lamellae in pearlitic steels improve wear resistance by acting as a barrier to dislocation propagation and thus strengthening the steel. Pearlite also has great strain-hardening potential through stabilizing ferrite plasticity by elastically deformed cementite at early deformation stages [18,19]. With the increasing number of rolling cycles, the interlamellar spacing reduces, subgrains and nanoscale grains form, leading to the Hall-Petch strengthening [20–22]. Consequently, the surface hardness increases, and wear performance is improved [23,24].

The reason for a slightly higher weight loss of hypereutectoid pearlitic steel during rolling (Fig. 2.6a) is related to the tendency of the grain boundary cementite to fracture [27]. A similar issue is partially responsible for the severe weight loss in steels containing spheroidized cementite. Large cementite inclusions are more difficult to deform plastically than thin lamellae and often act as crack nucleation sites and therefore increase the material removal rate during wear [25–27]. In the steels with spheroidized cementite, the strain hardening potential is much lower than for pearlitic steels, which is another reason for worse wear resistance (Fig. 2.6a). In bainitic steels, fine cementite particles prohibit dislocation movement, and the ferrite matrix contributes to better ductility than in

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martensitic steels. As a result, the wear performance of bainite can reach that of pearlite [83,84].

The deformation of multiphase steel microstructure at high strains (high cycle fatigue wear) is often accompanied by cementite dissolution as well as the white etching layer/area formation (WEL/WEA). On the one hand, cementite dissolution results in some degree of solid solution strengthening of the surrounding carbon-supersaturated ferrite due to severe plastic deformation [15,86–90]. On the other hand, the formation of WEL/WEA is associated with fatigue cracks responsible for rapid wear failures [8,9,16,28]. The microstructure evolution and cementite deformation and decomposition are either partially responsible for the WEL/WEA [9] or the leading cause of this transformation [91].



Fig. 2.6. Wear responses of steels with different microstructures and cementite fractions. (a) Wear weight loss of pearlite (pearlitic steel), hypereutectoid pearlitic steel (cementite steel), and spheroidized cementite in the martensite matrix (tempered martensite steel), as well as spheroidized cementite in the ferrite matrix (spheroidal carbide steel) during a rolling contact wear experiment. (b) Wear volume loss of pure iron, S45C (7 vol. % spheroidal cementite in the ferrite matrix), and three sintered ferrite-cementite samples (50, 75, and 100 vol.% cementite) during the pin-on-disc wear test. The inset shows the dependence of the Vickers hardness H_V on the volume fraction of cementite in the samples. Adapted from [23,30].

The volume fraction of cementite in steel, as well as the deformation behavior of cementite, affect the wear resistance. Sasaki et al. [30] compared the wear properties of specimens containing different fractions of cementite for various apparent applied pressures. (Fig. 2.6b) The samples of pure iron, S45C (7 vol. % spheroidal cementite in a ferrite matrix), and three sintered ferrite-cementite samples (50, 75, and 100 vol.% cementite) were

subjected to the pin-on-disc wear test against the abrasive alumina paper. The Vickers hardness of the samples (inset on Fig. 2.6b) increases nearly linearly with the increase of cementite volume fraction. However, the resistance to wear is not entirely proportional to the hardness of examined materials. The wear volume loss significantly decreases with higher cementite content until the volume fraction of cementite reaches 50%. Compared to the 50 vol.% cementite sample, the 75 vol.% and 100 vol.% samples demonstrate only a minor improvement in wear resistance (Fig. 2.6b).

Moreover, with the increase of the applied pressure from 0.61 MPa to 1.23 MPa during the wear experiment, the 100 vol.% cementite sample demonstrated more severe abrasion than the 75 vol.% cementite sample (Fig. 2.6b). This deviation is attributed to the change of the wear mechanism in the samples with a cementite fraction higher than 75 vol.%: instead of the dominating ductile chip formation at lower applied pressures (<0.15 MPa), brittle fracture tends to occur at higher applied pressures (>0.31 MPa) [30].

In Zheng et al. [31], similar conclusions were made for the three-body wear experiments. The authors compared the wear resistance of the pure iron and samples with 7.83 vol.% cementite (eutectoid pearlite), 18.56 vol.% cementite (cementite in pearlite matrix), 49.21 vol.% cementite (cementite in pearlite matrix), 81.75 vol.% cementite (cementite with ferrite inclusions) and 100 vol.% cementite. The samples were moved in a block-onring configuration against a steel countersurface covered with SiC particles at different applied pressures. The wear resistance greatly improved up to 18.56 vol.% cementite composition and remained relatively constant with higher cementite content [31]. At higher applied pressure of 0.098 MPa, brittle fracture in pure cementite sample leads to a higher wear weight loss than for the other samples with lower cementite content.

The applied pressures reported in Sasaki et al. [30] and Zheng et al. [31] are much lower than the contact pressures required to produce deformation in cementite by the microscale wear experiments in this thesis. It should be noted that the details for applied pressure calculations were not provided in the mentioned studies. However, the principles of pin abrasion, as well as block-on-ring experiments, differ considerably from the microscale wear experiments conducted in this thesis. Despite the experimental differences, the first experimental studies on bulk cementite have demonstrated the high importance of investigating the deformation behavior of cementite under various wear conditions.

2.2 Review of tribological techniques

2.2.1 Nanoindentation

The indentation experiment is commonly used to study the near-surface mechanical properties of materials. During the indentation experiment, a hard body of specific geometry (indenter) is pressed with a specified normal force against a surface of the tested sample to create a residual impression. The normal force is then divided by the projected contact area to obtain the mean contact pressure between the indenter and the material, i.e., indentation hardness. Different indentation methods employ different indenter tips, loading conditions, and hardness scales. The traditional macroscale and microscale methods include Brinell [92], Rockwell [93], Vickers [94], and Knoop [95] hardness tests. The measured hardness values are method-specific and often need to be rescaled for comparison. Tabor [43] later deduced a simple empirical relation between the indentation hardness and yield strength for metals, which has been used as an alternative method to determine the yield strength in an uniaxial tensile test. This relation presumes that only one-third of the mean contact pressure (hardness) participates in the plastic deformation due to the plastic flow criteria.

The development of the nanoindentation method (instrumented indentation testing or depth-sensing indentation) by Doerner and Nix [96] followed the improvement of the depth-sensing indentation systems [97,98]. While the previously established indentation hardness methods involve optical imaging of the residual impression, the nanoindentation method allows for the simultaneous calculation of the projected contact area based on the continuously recorded vertical displacement of the indenter. In addition, the applied normal force is recorded during both loading and unloading segments (Fig. 2.7a). Consequently, the nanoindentation method has proven to be a more accurate technique for quantifying the near-surface mechanical properties.



Fig. 2.7. The Oliver-Pharr method. (a) Force-displacement curve with marked parameters measured during nanoindentation experiment. (b) Parameters characterizing the contact geometry during loading and unloading segments. [99]

Based on the method by Doerner and Nix [96], Oliver and Pharr [99,100] introduced a modern technique for determining the hardness and elastic modulus based on the forcedisplacement data obtained during nanoindentation (Fig. 2.7). During the quasi-static and frictionless indentation into the elasto-plastic material, the loading curve includes both elastic and plastic displacement contributions, whereas the unloading curve is purely elastic (Fig. 2.7a). According to the Oliver and Pharr method, the contact stiffness *S* is defined from the slope dF_N/dh of the elastic unloading curve. The contact stiffness can also be extracted using the Sneddon relation [101]:

$$S = \beta \frac{2}{\sqrt{\pi}} E_{eff} \sqrt{A_I} , \qquad (2.1)$$

where E_{eff} is the effective modulus, A_I is the contact area, β is a dimensionless parameter. Based on this relation, the elastic modulus of the sample E_{sample} can be quantified. The effective compliance $1/E_{eff}$ combines the compliances of the indenter tip $1/E_{tip}$ and the sample $1/E_{sample}$ by analogy to a series of springs:

$$\frac{1}{E_{eff}} = \frac{(1 - v_{tip}^2)}{E_{tip}} + \frac{(1 - v_{sample}^2)}{E_{sample}},$$
(2.2)

 v_{tip} , v_{sample} are Poisson's ratios for the nanoindenter tip and the specimen, respectively.

At the maximum normal force $F_{N,max}$ The contact area A_I is determined using contact depth h_c through the area function F (Fig. 2.7b):

$$A_I = F(h_c) \,. \tag{2.3}$$

The contact depth h_c is obtained from the penetration depth h, the unloading stiffness S, and the maximum force $F_{N,max}$ according to $h_c = h - \varepsilon F_{N,max}/S$ for sink-in materials (amount of sink-in $h_s = \varepsilon F_{N,max}/S$) and $h_c = h$ for ductile materials, where ε is a geometrical constant ($\varepsilon \sim 0.72$ for conical and Berkovich indenters) [33,102].

The area function depends on the indenter tip geometry and is calibrated prior to the experiment. One of the standard nanoindenter tips is the Berkovich indenter – a geometrically self-similar pyramidal tip with three sides and a half-included angle of 65.3° .

For the ideal Berkovich nanoindenter geometry, the contact area function is given by:

$$A_I = 24.56 h_c^{\ 2}. \tag{2.4}$$

Due to the difference between the ideal and real geometry, such as tip rounding, the area function changes to:

$$A_{I} = 24.56h_{c}^{2} + m_{1}h_{c}^{1} + m_{2}h_{c}^{1/2} + \dots + m_{8}h_{c}^{1/128}$$
(2.5)

Here, $m_1..m_8$ are the constants determined by curve-fitting during area function calibration. Using the projected contact area and normal force, the nanoindentation hardness is defined as:

$$H_I = \frac{F_{N,max}}{A_I} \quad . \tag{2.6}$$

The Oliver-Pharr method [99,100] has been adopted as a standard ISO 14577 [103] and is commonly employed for small-scale measurements of elastic modulus and hardness of materials. In addition, nanoindentation has been widely used to inspect many material-related phenomena, such as fracture toughness, phase transformations, strain hardening, and high-temperature creep deformation.

Pethica and Oliver [104,105] have also developed an extended nanoindentation technique named continuous stiffness measurement (CSM). The CSM method generates small controlled loading-unloading oscillations on the loading curve and uses the data obtained
during the unloading stage of oscillation to measure the contact stiffness. Based on the stiffness data continuously recorded throughout the entire loading curve, the hardness and elastic modulus are reported as functions of penetration depth. Compared to the conventional single loading-unloading experiment that provides a single data point, the CSM technique allows for obtaining much larger amounts of data from a single nanoindentation measurement. This method was found to be especially beneficial for the studies of the nm-thick films that require ultra-low nanoindentation depths. The detailed measurement protocol used in this thesis during nanoindentation is provided in section 3.2.

2.2.2 Microscale sliding wear

For ductile materials, wear modes are often classified into adhesion, abrasion, surface fatigue, and tribochemical reactions. Abrasion is the material removal due to the relative motion of two bodies in contact, for instance, during sliding wear [106]. Since the equipment of indentation instruments with lateral displacement motors and tangential force probes, controlled sliding wear experiments were carried out to study materials' response to abrasion. Like indentation, the wear experiment produces a permanent impression, i.e., wear track groove, due to the contact of two bodies. Compared to the nanoindentation, the indenter tip also moves across the surface, and a corresponding tangential force F_T arises during the wear experiment (Fig. 2.8a). The normal force F_N either constantly increases at a specified rate or remains constant through the entire wear track distance. Therefore, the wear experiment is simultaneously probing the material's resistance to deformation in normal and lateral directions.

The micro-scale single-pass wear experiment is capable of replicating the single asperity contact, i.e., two-body abrasion. By inspecting the wear track groove and wear debris morphology, the predominant abrasive wear mechanism can be determined, e.g., plastic plowing or cutting [32]. Some first quantitative abrasion models assumed pure cutting in single-track wear motion [107,108]. Subsequently, pile-ups and chips in front of the wear track as well as on the sides were observed in different proportions based on the experimental conditions [109–111].

To assess the wear track groove formation and its elastic and plastic contributions, the penetration depth is typically recorded and plotted as a function of the wear track distance (Fig. 2.8b). A measurement protocol of the microscale single-pass wear experiment includes three segments: pre-scan, wear segment, and post-scan. The deformation is

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induced only during the wear segment, whereas the pre-scan and post-scan are performed at the minor normal force to study the topography of the undeformed and deformed surface, respectively. By analyzing the data obtained from the pre-scan, the surface roughness can be accounted for, and surface tilt can be compensated. The elastic recovery of the wear track and the remaining plastic depth are determined based on the differences between the three segments. In addition, the front pile-up height can be quantified based on the post-scan data [37,112,113]. A detailed description of the threesegment wear measurement protocol is given in section 3.2.



Fig. 2.8. (a) Schematic of a sliding wear experiment. (b) Typical curves of penetration depth as a function of the sliding distance during the pre-scan, the wear segment, and the post-scan of the microscale wear experiment with a constant normal force on austenitic steel. Blue and red areas mark elastically recovered and plastic depths, respectively. Adapted from [37,114].

Normal and tangential forces are continuously recorded during the wear segment. As a result, the friction coefficient is evaluated as a ratio of the tangential force F_T to the normal force F_N (Fig. 2.8a) to investigate the friction behavior of the material. For instance, in the ramp-up force wear experiments on coated surfaces, the abrupt change in friction coefficient or tangential force can be associated with the damage or delamination of a coating [115,116]. To determine the loading conditions at which the failure occurred, the friction coefficient or tangential force is plotted as a function of normal force or wear track distance.

In addition to the single-pass wear experiment, a multi-pass test is adopted to analyze the wear response of materials under low cycle contact fatigue conditions. During multi-pass wear, deformation is induced by producing multiple wear tracks with the indenter moving either repeatedly in one direction or reciprocally. The surface material is removed as wear debris during the initial cycles and induces three-body wear conditions during the later cycles. The relative abrasion resistance of materials can be characterized by comparing

the quantified material volume or weight loss during wear experiments under the same loading conditions [117,118]. However, a comparison of wear volume/weight losses between studies that employ different normal forces, wear velocities, and indenter geometries is difficult. Instead, scratch hardness obtained from the single-pass microscale wear test is often used as a quantitative measure to evaluate the material resistance to wear and to model plastic plowing [39,41,43,119].

Before the first indentation hardness methods were developed and formalized, the hardness scale was based on wear tests. Friedrich Mohs [119] examined the ability of ten materials to leave wear marks on each other and then placed these materials in the ascending order according to their hardness, i.e., from talc to diamond. Later, Tabor stated that the indentation hardness scale was related to the Mohs scale: each step on the Mohs scale correlated to an increase of indentation hardness by approximately 60%, except for the last step from alumina to diamond [120]. Williams [39] proposed two hardness properties that can be measured based on the wear experiment at constant normal and tangential forces: scratch hardness H_S and plowing hardness H_P (Fig. 2.9). The measurements of both scratch and plowing hardness allow for a more detailed examination of wear resistance. The scratch hardness H_S is analogous to the indentation hardness H_I , since both values are calculated as normal force divided by the contact area projected on the sample surface:

$$H_S = \frac{F_N}{A_S},\tag{2.7}$$

This method was later adopted as a standard test method for scratch hardness ASTM G171-03 [121]. Plowing hardness quantifies the wear resistance in the lateral direction [39] and is defined as a tangential force divided by the contact area projected in the lateral direction:

$$H_P = \frac{F_T}{A_P},\tag{2.8}$$

According to the model of Williams, the wear contact area can be deduced from the wear track width (Fig. 2.9) [39]. The width is conventionally measured using optical inspection of the wear tracks. Therefore, this measure is similar to those macroscale and microscale indentation methods that involve optical imaging of residual impressions. Alternatively, the wear track groove parameters can be measured via atomic force microscopy (AFM) or confocal microscopy. Depending on the indenter shape (conical, pyramidal), the projected

contact areas in normal and tangential directions have different shapes. The majority of the wear experiments are conducted using conical tips with hemispherical tips that do not require a specific alignment regarding the sliding direction.



Fig. 2.9. Schematic for the measurement of the scratch and plowing hardness based on the wear experiment with a Vickers indenter. (a) Wear track groove with marked directions of normal and tangential forces and a wear track width. (b) Projected contact areas in vertical and horizontal directions. Adapted from [39].

Other hardness definitions using the wear experiments include hardness based on the force balance model [35,110,122–124] and hardness calculated as a ratio between the work of deformation and the volume of the wear track groove [125,126]. These definitions represent different mechanical processes than the scratch hardness given by Williams [39], differ from the Force-Area-relation of indentation hardness, and are often more cumbersome to determine experimentally.

2.2.3 Challenges of linking indentation and wear

In some applications at the micro-and nanoscale, the wear experiment proved to be more favorable than indentation. For instance, the penetration depth during nanoindentation of thin films is typically limited by 10% of the film's thickness to reduce the influence of the stiff substrate [127,128], as opposed to 30% for the nanoscale wear test [129]. The local influence of surface roughness, individual grain orientation, grain boundaries, as well as uneven film thickness can be reduced if the wear track is sufficiently long to average out their contributions. In the field of coating-substrate adhesion research, the ramp-force wear experiment is often employed to determine the critical normal force at the onset of coating delamination, which is accompanied by a rapid change in the friction coefficient [115] and

scratch hardness [130]. Several models establish the relationships between the critical force and the fracture energy of the coating-substrate interface as well as correlate the critical force with hardness and film thickness [131–133]. Wear experiments with varying normal forces and sliding velocities also proved effective for the analysis of plastic deformation, crack formation, and micro-abrasion in brittle glasses [125,134].

A limited number of studies are dedicated to understanding the transition from indentation to plastic plowing. Goddard and Wilman [110] have shown that the friction coefficient is larger at the start of the wear track until the wear mechanisms reach a stable regime. The transition is also accompanied by the penetration depth increase (Fig. 2.8b, 2.10), which is not related to the experiment protocol, i.e., whether or not indentation is followed by intermediate unloading and reloading [37]. Kareer [135] has conducted microscale wear experiments on copper with a Berkovich tip in edge forward and face forward orientations and correlated the magnitude of the initial depth increase with the fraction of the indentation to the wear contact area. For viscoelastoplastic polymeric fibers, Cayer-Barrioz et al. [36] observed only a gradual decrease of penetration depth after the initial depth increase in nanoscale wear experiments at ultralow normal force. Tayebi [122] has shown that the penetration depth did not decrease after reaching the maximum value in fused quartz: this behavior of fused quartz is fundamentally different than that of metals. In numerical plowing models [136–138], the penetration depth increase during the transition from indentation to wear is observed as well. It was found that the magnitude of penetration depth decrease and the length of the transition region depend on the normal force, the tip shape, and its orientation.

The mechanisms that lead to the initial depth increase and subsequent depth decrease were discussed in several studies. The initial depth increase is associated with the change in the total force on the sample due to added lateral force [122]. As the indenter tip loses contact with the back half of the asperity, the change in contact area requires the increase of the frontal contact area to support the evolved total normal and tangential force during wear [135,137]. The gradual depth decrease in wear experiments on viscoelastoplastic polymeric fibers was attributed to a combined effect of viscoplasticity and interface friction [36]. Although elastic recovery was explicitly examined for the case of wear in polymers [139–141], its effect on the penetration depth evolution during the transition from indentation to wear was not addressed. A proposed explanation for the subsequent depth decrease is based on the pile-up development in front of the indenter tip [137].



Fig. 2.10. Schematic depth curve for a wear experiment. Initially, the wear depth increases, followed by a subsequent depth decrease during the transition from indentation to the steady-state region of plastic plowing.

Using the scratch hardness as a quantitative measure for the material resistance to plastic plowing [39], numerous material-related phenomena were examined, such as size effects [35,142,143], temperature-dependent deformation behavior [144], and strengthening mechanisms [145,146]. Since the basic principles of nanoindentation and wear experiments are similar, it is often believed that there is a link between nanoindentation and scratch hardness. Nonetheless, no direct relation was found previously. While the static indentation hardness assumes the absence of friction between the indenter and material [1], the scratch hardness is strongly related to the interfacial shear stress that arises during the dynamic wear test [122]. This strong dependence on the friction coefficient complicates the relation of scratch hardness-yield stress relation similar to Tabor's relation for indentation in metals.

The present research demonstrates the discrepancy between indentation hardness H_I and scratch hardness H_S . Brookes et al. [41] used conical indenters with different apex angles to quantify the ratio between indentation hardness and scratch hardness in a number of materials. It was shown that the hardness ratios H_I/H_S were within the range of 0.59 to 1.72 and decreased with an increase in the indenter apex angle. De Beurs et al. [147] conducted indentation and wear experiments using Vickers indenters on a laser-treated steel surface. They stated that the induced stress state during a wear test leads to martensitic transformation and consequently to a higher scratch hardness than the indentation hardness measured using a spherical tip to the Vickers hardness of the 304 stainless steel by applying a linear relation $H_I/H_S = 0.77$. They argued that the plowing behavior during the wear test was responsible for the differences between Vickers hardness and scratch hardness. A different relation with $H_I/H_S = 1.43$ between Vickers hardness and scratch hardness was defined by Ichimura and Rodrigo [149] for TiN

coatings deposited on different substrates. Graça et al. [142] examined size effects in the Ni-Co system by performing indentation and wear experiments at several penetration depths. They used a Vickers tip for the two sets of microindentation experiments and a Rockwell conical tip for the microscale wear tests. For nanoindentation and nanoscale wear experiments, a three-sided pyramidal diamond tip for AFM was used. Graça et al. demonstrated at the microscale that the ratio of indentation hardness to the scratch hardness H_I/H_s varied from 0.43 to 0.86, contrary to nanoscale experiments for which the hardness ratio is much larger (0.94 to 1.72). It was concluded that the measurement depth affects the hardness-depth scaling more in indentation than in wear. In the work of Sawamura and Wondraczek [126], the scratch and indentation hardness measured by Berkovich indenter were compared for a wide selection of glasses, and no proportionality between scratch hardness and indentation hardness was found. The authors pointed out that the ratios between indentation hardness and scratch hardness can differ even for materials with very similar indentation hardness. Recently, Kareer et al. [35] compared the nanoindentation hardness to the scratch hardness of single-crystal copper using a Berkovich tip. For the wear experiments, edge forward and face forward orientations were employed. The indentation hardness was demonstrated to be smaller than the scratch hardness in most cases, except for the scratch hardness in the edge-forward orientation and penetration depths less than 100 nm. Hence, this comparison shows that different indenter tips and normal forces were used to measure the scratch hardness (in addition to different methods to determine the scratch hardness as detailed in the following), and no clear relationship to microindentation/nanoindentation hardness could be established.

The investigation of the relation between scratch hardness and indentation hardness or yield strength is further complicated by the variety of scratch hardness definitions. While the standard scratch hardness [121] is based on the definition proposed by Williams [39], differences arise because of the absence of a unified measurement protocol for the wear track width. This absence of a unified protocol has led to the groove width being evaluated using different critical points while presuming the same name: wear track width. The most frequently used definition of the wear track width is the distance between the highest points of the side pile-up [40,134,147,150–152] in the profile that is perpendicular to the wear track. If the residual wear track is very shallow, the side pile-up height may be similar to the inevitable surface roughness, and thus the scratch hardness has a large scatter for small penetration depths. In this case, the wear track width may be determined from a distance between the points with a significant groove slope [123]. Another wear track width measure assumes the circumference of the contact region at the surface level, i.e., surface mean height [142]. In the article of Useinov et al. [153], the authors proposed to measure

the width by incorporating the depth scans along the sliding direction before, during, and after the wear experiment. Based on the depth scans, they define a surface elevation at which the contact width is measured. Several researchers also derive the projected contact area from the penetration depth as well as tip geometry and its orientation with respect to the sliding direction [35,154].

3. Methods

3.1. Materials and sample preparation procedures

3.1.1. Cementite samples

The first part of this thesis (Chapters 4 and 5) mainly focuses on the tribological behavior of bulk cementite (Fe₃C). Bulk cementite samples (courtesy of Prof. Y. Todaka of the Toyohashi University of Technology) were produced using spark plasma sintering. The initial high-purity Fe (99.9%, 150 μ m size) and C (99.9%, < 20 μ m size) powders were mixed in a 3:1 ratio and mechanically alloyed for 20 h on a vibration ball mill in an argon atmosphere. The ball-to-powder weight ratio was 100:1. After mechanical alloying, the powders underwent spark plasma sintering to produce bulk cementite samples. The temperature was increased at a heating rate of 2.17 K/s until 1173 K (900 °C) was reached. The sintering was performed in a vacuum under a load of 50 MPa for 15 min. The fabricated samples with \emptyset 20 x 1 mm dimensions were then cooled inside the furnace. The cementite fabrication is described in detail in [29].

Cementite is present in 94.5 vol.% (~95 wt.%) with an average grain size of 436±18 nm, according to the XRD measurements after sample metallographic preparation. Small fractions of iron (2.9 vol.% ~ 3 wt.%) and iron oxide FeO (2.6 vol.%, ~2 wt.%) were also detected. Some graphite that did not transform during the sintering of the cementite sample was observed in the SEM (Fig. 4.1, section 4.2.1.1), TEM, STEM images, diffraction patterns, and EDS measurements (Fig. A1-Fig. A3 in Appendix A). In the original work by Umemoto et al. [31], a relative sample density of 98% was reported. Hence, 2% porosity is present in the sample.

3.1.2. Materials for studies of the links between indentation and wear

The second part of this thesis is based on the two case studies of relations between indentation and wear experiments, for which different materials were selected. For the analysis of the wear track groove evolution during the transition from indentation to plastic plowing (Chapter 6), austenitic steel (γ -Fe), copper (Cu), and cementite (Fe₃C) were chosen as materials with different macroscale mechanical properties (e.g., hardness, elastic modulus). In order to carry out several wear experiments in the single austenite grains, two large grains with [001] and [111] normal orientations were chosen as characteristic scenarios.

For the study of the relationship between nanoindentation and scratch hardness (Chapter 7), materials with a wide range of hardness and Young's modulus values were chosen to account for different materials' behavior during nanoindentation and wear testing on the microscale: sink-in and pile-up behavior. To this end, polycrystalline aluminum (AI), copper (Cu), soda-lime glass (SLG), as well as single-crystal silicon (Si), and cementite (Fe₃C) were examined. The face-centered cubic metals aluminum and copper are ductile and deform plastically by slip and twinning [155] while forming pile-ups. Silicate glasses, such as soda-lime glass, are mostly elastically deforming (sink-in behavior) but can exhibit plastic densification if a confined volume is deformed [156]. The plasticity of cementite is limited, given its complex orthorhombic crystal structure. However, cementite lamellae in pearlitic steel are partially capable of deforming plastically (section 2.1.1). The inhomogeneity of the cementite microstructure does not cause significant standard deviations in measured mechanical properties because of the small fraction of precipitates and their small size relative to the tested volume and the indenter tip radius. Silicon shows a brittle behavior at room temperature and naturally has a very limited number of dislocations [157]. Therefore, the materials differ in mechanical properties (e.g., Young's modulus and hardness) and have fundamentally different deformation behavior. By performing the tests on aluminum, copper, soda-lime glass, silicon, and cementite, it is possible to systematically advance from ductile materials that pile-up around the indenter to elastically deforming materials that show sink-in behavior during indentation.

3.1.3 Sample preparation procedures

The accuracy of the nanoindentation and wear measurements significantly relies on the surface quality as well as the absence of the residual deformation after mechanical grinding and polishing. Therefore, the samples were prepared carefully to minimize the surface roughness and deformation, especially the soft aluminum and copper samples. The details for the sample annealing and metallographic preparation procedures are given in Table 3.1. The average surface roughness was determined after metallographic preparation by the topography line pre-scan at 0.15 mN force (section 3.2) via the 5 μ m sphero-conical tip prior to the microscale wear experiments.

	Annealing	Metallographic preparation	Final surface roughness [nm]
Fe₃C	- (used as received)	Grinding with SiC paper starting from	10±2
γ-Fe	The as-received sample was annealed at 1200 °C for roughly one week [37].	gradually proceeding up to grade P4000,	6±1
Cu	The as-received sample was annealed at 600 °C for one week to obtain a coarse polycrystalline microstructure.	polishing with 3 μm and 1 μm polycrystalline diamond suspension	18±2
AI	The as-received sample was annealed at 280 °C for 24 hrs to attain a coarse polycrystalline microstructure	(Struers) and the colloidal silicon oxide polishing suspension (OPS, Struers)	34±3
Soda-lime glass	- (used as received)	-	4±1
Si	- (used as received)	-	5±1

Table 3.1. Sample preparation procedures.

3.2. Tribological experiments

3.2.1 Nanoindentation and single-pass microscale wear

The majority of nanoindentation and wear experiments for this thesis were carried out in the G200 Nanoindenter (Agilent, Keysight, KLA, Fig. 3.1a). This nanoindentation instrument allows for automated data collection and near-surface properties analysis according to the Oliver-Pharr nanoindentation method [100] (section 2.2.1). The main components are the indenter head, the motorized stage, and the optical microscope (Fig. 3.1b) [33,158]. In order to isolate the system from the external vibrations and ensure thermal stability, the apparatus is placed on a vibration table inside the isolating cabinet.



Fig. 3.1. (a) The KLA nanoindenter and (b) schematics of its major components. Adapted from [33,159].

The normal force in the range from 0 to 500 mN (sensitivity 50 nN) [158] is produced via the coil-magnet assembly and is transferred to the indenter tip through the indenter shaft. The force can be imposed on the sample either by using the single-loading-unloading method or the continuous stiffness measurement (CSM) method, for which a small sinusoidal signal is added to the DC signal. The vertical displacement of the indenter tip is measured by the capacitive displacement gauge (resolution of ~0.01 nm [158]). Thus, the system can continuously measure and control the applied force and displacement through a closed feedback loop between the two branches. The indenter column is supported by the two sets of leaf springs that stabilize it and increase its lateral stiffness. During the wear experiments, the lateral force probes measure the indenter shaft deflection in the x- and y-directions relative to the initial position. Based on the deflections of the column and the spring stiffness, the lateral force up to 250 mN with 2 μ N [158] resolution along the wear track is recorded.

The sample is rigidly adhered to the sample mount inserted into the sample holder, which in its turn moves with the stage in x- and y-directions via piezoelectric motors (accuracy in the order of 10 nm). The stage can move with velocity from 100 nm/s to 2 mm/s to produce wear tracks with lengths up to 100 mm. The movement in the z-direction is limited and is controlled manually during sample mounting. In order to navigate to the sample or identify the tested area, the instrument is equipped with a top-down optical microscope controlled by the software. A microscope-to-indenter calibration is required to ensure that the microscope and the indenter positions correspond to each other. The detailed specification of the G200 nanoindenter can be found in [33,158].

The hardness and elastic modulus were measured using a diamond Berkovich indenter (Synton-MDP) with a tip radius of about 50 nm, using the CSM technique and in agreement

with the ISO 14577 [103]. To reduce measurement artifacts and obtain reliable results, the nanoindentation measurements are performed multiple times. For the relatively homogeneous materials, a minimum of 5 indents is required. The environment has a nearly constant temperature of ~22 °C. Prior to the measurements, the indenter tip area function was calibrated on a fused silica sample. The nanoindentation test protocol includes the following steps:

- The indenter moves towards the sample surface until contact is established. This contact event is determined by the rapid increase in contact stiffness that fulfills the surface approach sensitivity criterion (set in N/m). Both the surface finding step and the following thermal drift stabilization are carried out at a certain distance from the test region.
- 2) The thermal drift is stabilized, while keeping the indenter tip in contact with the surface. Then, the fluctuations of the penetration depth are measured over time. When the thermal drift decreases to less than 0.05 nm/s, the indenter tip withdraws from the surface, and the test segment is initiated.
- 3) The indenter moves to the specified test location and approaches the surface from a distance of 1000 nm with the velocity of 10 nm/s until contact is established again.
- 4) The normal force F_N or displacement *h* is increased to the target maximum value while keeping a constant strain rate (dh/dt)/h of e.g., 0.05 s⁻¹. The CSM technique implies additionally harmonic oscillation with a displacement range of ~2 nm at a frequency of 45 Hz.
- 5) The maximum normal force is held constant for several seconds to allow for verification that the creep of the material is minimized.
- 6) The indenter unloading occurs at the same rate as loading.

Further experimental details for nanoindentation experiments are given in Table 3.2.

	Sample	Target depth [µm]	Tests per batch	Remarks
Chapter 4	Fe₃C	1.2	5	Nanoindentation performed on undeformed cementite and smooth non-fractured surface regions deformed by the multi-pass experiment
Chapter 7	AI	2	5	Higher target depths used to investigate the entire domain of the possible indentation size effect (ISE) in aluminum and copper
	Cu			
	Soda-lime glass			
	Fe₃C	1		
	Si			

The wear experiments were performed under normal force control using diamond spheroconical indenters (Synton-MDP) with different tip radii. By employing tips with rotational symmetry, we exclude the effect of indenter orientation relatively to the wear direction [35]. However, due to the directional anisotropy, the wear track groove evolution and the corresponding wear response depends on the relative orientation between the sliding direction and crystallographic orientation of the individual grains. Therefore, in order to average the effects of surface roughness and individual grain orientation, batches of 3 wear tracks with 100 μ m and 400 μ m lengths at the same loading conditions are conducted. Since the silicon sample is a single crystal, the influence of the directional anisotropy during wear cannot be excluded. For the studies of the microstructure evolution due to wear or to investigate the individual grain response to tribological loading, single wear tracks of smaller length are sufficient. Similar to the nanoindentation, the wear tests were conducted at the constant temperature (22 °C ± 0.2 °C) without lubrication. Humidity was not controlled but stayed between 30% RH and 60% RH. The wear experiment protocol can be described as follows [37,160]:

1) The indenter moves at the specified velocity towards the sample surface until the contact is established at a certain distance from the test region.

- 2) Thermal drift is stabilized when it decreases to less than 0.15 nm/s. Then the indenter withdraws from the surface, and the pre-scan segment is initiated.
- 3) During the pre-scan segment, the indenter approaches the surface at the specified test location until contact is reached and then scans the surface to analyze the initial surface topography and the surface tilt. The profiling normal force of 0.15 mN is minor and does not produce any plastic deformation as verified by a subsequent SEM imaging. An additional 10-20% of the wear track length is recorded in the front and back of the wear track in order to be correctly superimposed with the wear and post-scan segments.
- 4) At the beginning of the wear segment, the indenter moves back to the specified test location and approaches the surface until contact is reached. Then the abovementioned 10-20% length before the wear track is scanned using the profiling force.
- 5) When the tip reaches the specified position of the wear track start, the lateral movement stops, and the tip indents the sample until a pre-defined normal force is reached. The indenter holds a constant normal force constant for several seconds, fully unloads, and reloads to the pre-defined force again.
- 6) Then the sample moves laterally with constant sliding velocity and normal force for a specified wear track distance, i.e., wear segment. After the specified length of the wear track is reached, the indenter unloads to the profiling force and scans the additional 10-20% of the wear track length in the back of the wear track.
- 7) The last step is profiling of the wear track surface by a post-scan using the profiling normal force of 0.15 mN to provide information on the elastic recovery and pile-up height. The additional 10-20% in the front and back of the wear track are measured as well.

Based on the three measured segments, the penetration depth as the difference between the pre-scan and the wear segment is quantified (Chapters 6, 7). In order to determine the average penetration depth within the steady-state region of the wear track, the first and last 10% of the wear track length are excluded.

Other experimental details for the single-pass microscale wear experiments are given in Table 3.3.

	Sample	Tip radius [µm]	Normal force [mN]	Wear velocity [µm/s]	Wear length [µm]	Tests per batch	Remarks
Chapter 4	Fe₃C	5	100	10	100	1	Normal force leads to Hertz pressure of 31 GPa (El. moduli and Poisson ratios: 141 GPa and 0.07 for the tip, 204 GPa and 0.36 for Fe ₃ C) [161]
Chapter 5	Fe₃C	5	100	10	100	1, 200	A 200 wear-track-array for the XPS
Chapter 6	γ-Fe [001], [111]	5	40	1	2-20	1	Two test sets with and without a 5 s hold after the wear segment
	γ-Fe	5	5-100		100		
	Cu	5, 20	5-200	10	400	3	-
	Fe ₃ C	5, 20	5-200				
Chapter 7	AI	5, 20	5-200	10		3	
	Cu	5, 20	5-200				
	Soda- lime glass	5, 20	5-200		400		-
	Fe₃C	5, 20	5-200				
	Si	5, 20	5-200				

Table 3.3. Experimental details for single-pas	ss microscale wear experiments.
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3.2.2 Models for contact area and hardness

In order to determine the relations between nanoindentation hardness and scratch hardness (Chapter 7), we determine the corresponding contact areas during the nanoindentation and microscale single-pass wear through the contact depth and wear track groove width parameters.



Fig. 3.2. Schematic of the projected contact area (grey). a) Contact area during nanoindentation with a Berkovich tip and the related contact depth h_c . b) Scratch contact area based on contact depth and sphero-conical tip geometry. Depending on whether the spherical or conical part of the tip is used, a different analytical model is employed. c) Typical surface profile perpendicular to the wear direction measured by confocal microscopy. Three wear track width measures were evaluated for the sphero-conical tip.

3.2.2.1 Nanoindentation contact area definition

The nanoindentation contact area function for the Berkovich nanoindenter (Fig. 3.2a) is based on the Oliver and Pharr [99,100] method described in the section 2.2.1:

$$A_{I} = 24.56h_{c}^{2} + m_{1}h_{c}^{1} + m_{2}h_{c}^{1/2} + \dots + m_{8}h_{c}^{1/128} \quad . \tag{3.1}$$

The nanoindentation hardness is defined as

$$H_I = \frac{F_N}{A_I},\tag{3.2}$$

where F_N is the applied normal force.

We use the Nix-Gao model [162] to exclude the indentation size effect, i.e., hardnessdepth dependence that arises from the distribution of the geometrically necessary dislocations in metals [100,163–165], and calculate the macroscopic hardness of the studied materials:

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \ . \tag{3.3}$$

Here, *H* represents the hardness at a particular penetration depth *h*, H_0 corresponds to the hardness unaffected by geometrically necessary dislocations, i.e., macroscopic hardness, and h^* is a characteristic depth defined by the shape of the indenter and material parameters. The resulting linear relation between H^2 and 1/h is valid for microscale experiments on single crystal and polycrystalline metals [166,167]. However, the experimental data does not follow the Nix-Gao model when the penetration depth decreases below 100-200 nm [168–170]. This discrepancy is attributed to the indenter tip radius influence and the modified storage volume of geometrically necessary dislocations at the nanoscale [38,171]. The Nix-Gao model for metals (copper and aluminum) was used to determine the nanoindentation hardness $H_I = H_0$ from indentation tests in CSM mode for indentation depths above 200nm. Thereby, we analyze the influence of the nanoindentation size effect. The contact area during nanoindentation is evaluated from the indentet indentetion hardness H_0 and normal force.

3.2.2.2 Microscale wear contact area definitions

We use the scratch hardness H_S definition proposed by Williams [39] that defines the link between normal force and projected contact area A_S during steady-state wear (section 2.2.2):

$$H_S = \frac{F_N}{A_S}.$$
(3.4)

Contact area determined from contact depth

The scratch contact area A_s is linked to the average steady-state penetration depth h during wear, analogous to the Oliver-Pharr model for nanoindentation. In this investigation, the penetration depth for ductile materials is assumed to be equal to the contact depth h_c , based on the Oliver-Pharr method. For the present rotational-symmetrical tip, there is no relation between indenter tip orientation and sliding direction. Please note that for a Berkovich tip, the contact area depends on the orientation of the tip with respect to the sliding direction [35].

It is assumed that only the front half of the tip is in contact with the material [150], thereby forming a half-circular projected contact area for spherical and conical indenters (grey regions on Fig. 3.2b). This assumption was validated for materials that deform plastically, e.g., metals. In viscoelastic-viscoplastic materials, like polymers, the normal force was demonstrated to be partially supported by the tip rear [172,173].

The sphero-conical tip requires two expressions for the contact area during wear (Fig. 3.2b). At the transition depth h_t the spherical part transitions into the conical part:

$$h_t = R(1 - \sin \alpha), \tag{3.5}$$

Here, *R* is the radius of the tip-sphere, and α is the half-angle of the conical part. In this thesis, 5 µm and 20 µm tips with $\alpha = 60^{\circ}$ were employed, which results in transition depths of 2.5 µm and 5 µm, respectively. If only the spherical part of the tip is in contact with a surface ($h_c \leq h_t$), the area function $A_S(h_c)$ is represented as:

$$A_{S} = \frac{\pi}{2} \left[2Rh_{c} - h_{c}^{2} \right], \qquad (3.6)$$

where h_c is the contact depth. If the wear track depth h_c exceeds the transition point ($h_c \ge h_t$) and the material is also in contact with the conical part, then the area function is determined as follows:

$$A_{S} = \frac{\pi}{2} \left[tan\alpha \left(R \left(\frac{1}{sin \, \alpha} - 1 \right) + h_{c} \right) \right]^{2}.$$
(3.7)

Naturally, this contact area and contact depth evaluation includes elastic and plastic contributions.

Contact area determined from three wear track width parameters

On the other hand, the scratch contact area can be determined from the residual wear track width *[39]*, which assumes that the radius of the contact half-circle is half of the wear track width *w*:

$$A_S = \frac{\pi}{2} \left(\frac{w}{2}\right)^2. \tag{3.8}$$

The width evaluation is usually conducted by means of SEM, AFM, or confocal microscopy. The latter two methods allow to determine the width at a specific height. It is, therefore, possible to distinguish three wear track width definitions (Fig. 3.2c).

- The conventional wear track width definition is the distance of the highest points of the side pile-ups (w_{pile-up} [40,41]).
- One could presume that the indenter loses contact with the material at the point where the groove sidewalls have the maximum slope (dashed line on Fig. 3.2c)[123]. The distance between these locations on either side of the valley determines the width w_{max.slope}.
- If the side pile-up does not contribute to the load-bearing area, the wear track width $w_{surface}$ is determined at the initial surface level, i.e., surface mean line [142].

Analytical first-order approximation

We employ the Hertzian solution for the normal frictionless contact between the rigid sphere and elastic half-space [174] as a first-order approximation of the scratch contact area:

$$A_{S,Hertz} = \pi \left(\frac{3F_N R}{4E_{eff}}\right)^{2/3},\tag{3.9}$$

where E_{eff} is the effective Young's modulus, calculated from the expression:

$$\frac{1}{E_{eff}} = \frac{(1 - v_{tip}^2)}{E_{tip}} + \frac{(1 - v_{sample}^2)}{E_{sample}}.$$
(3.10)

Here E_{tip} , E_{sample} and v_{tip} , v_{sample} are Young's moduli and Poisson's ratios for the nanoindenter tip and the specimen, respectively. For the diamond indenter tip, a Young's modulus of 1141 GPa and Poisson's ratio of 0.07 were used.

3.2.3 Multi-pass wear

For the multi-pass wear experiments, a linear reciprocating macroscale tribometer was employed. The tribometer can introduce normal forces up to 350 N by adding specific dead weights and has two wear sensors. The reciprocating motion can be applied with

frequencies from 2 to 25 Hz for stroke lengths up to 20 mm. A detailed description of the instrument can be found elsewhere [175].

To determine the cementite microstructure evolution due to the multi-pass wear (Chapter 4), a sapphire sphere (Saphirwerk) with a diameter of 10 mm was reciprocally moved on the sample surface at a frequency of 25 Hz and a normal force of 230 N. The contact depth for a single stroke was calculated as 0.99 μ m. The reference Hertzian contact pressure was calculated as 3.3 GPa. Young's modulus of 345 GPa and a Poisson ratio of 0.3 were used for the sapphire tip, and 204 GPa and 0.36 were used for cementite. With a stroke distance of 5 mm, 2000 strokes were performed – resulting in an overall sliding distance of 10 m.

3.3. Microstructure and composition characterization

3.3.1 SEM and EBSD¹

Throughout this thesis, the microstructure of samples before and after tribological experiments was imaged in a Zeiss Gemini500 field emission SEM using Everhart-Thornley and Inlens secondary-electron detectors. The microscope was operating at 5 kV and a working distance of \sim 5 mm to obtain high-resolution images.

For crystallographic orientation measurements and the subsequent slip trace analysis of cementite after the single-pass wear experiment (Chapter 4), we conducted EBSD measurement on the side of the single-pass wear track groove. EBSD was performed using an EDAX detector with Hikari charged coupled device (CCD) in a Zeiss Auriga FIB-SEM workstation. The working distance and the voltage were set to 16 mm and15 kV, respectively. The scan step was selected to be 20 nm due to the small grain size in the cementite sample. Since the surfaces of interest are deformed and the grain size is small, a relatively low confidence index was expected during the Kikuchi pattern analysis. The wear track side areas scanned with EBSD were afterwards imaged via SEM while maintaining the same orientation of the imaged area. The crystallographic orientation was studied in the TSL OIM 7 software package. To identify the activated slip planes, a Mathematica script was applied to plot all possible slip traces for the crystallographic

¹ EBSD measurements and the subsequent slip trace analysis were performed by C. Tian, Max-Planck-Institut für Eisenforschung GmbH.

orientations of the examined grains and superimpose those orientations with the experimentally observed slip traces [176].

3.3.2 XRD²

Qualitative and quantitative phase characterization of the cementite sample, as well as grain size evaluation before and after multi-pass deformation, were conducted using XRD. The initial quantitative XRD phase analysis of the bulk cementite sample (Chapters 4, 5) was carried out in Bragg-Brentano geometry using a Bruker D8 Advance A25-X1 diffractometer with a Co-K α X-ray source (λ =1.79 Å) and LYNXEYE XE-T energy-dispersive 1D detector. The X-ray beam was extended in the Z direction (line focus), and the aperture slit was 0.3 mm. The XRD was operated at 35 kV and 40 mA for the 2 θ scan range from 20° to 130°. The quantitative analysis of phase fractions was carried out by Rietveld simulation [177] using the Bruker TOPAS 5.0 software. The fitting quality was defined by the weighted profile R - factor (Rwp) of 9,83%.

For the investigations on the worn surface after the multi-pass wear experiment (Chapter 5), a Rigaku SmartLab 9KW diffractometer with Cu-K α (λ =1.54 Å) radiation was employed. The measurement was conducted in the parallel beam/symmetrical scan geometry, with the micro-area CBOµ optics setup (125 µm beam, 0.5 mm length limiting slit) and HyPix 3000 2D detector. The voltage and current were 45 kV and 200 mA, respectively. The scan was conducted for the 2θ range from 20° to 120°, with a speed of 0.3°/min and 0.01° step. For the phase analysis, the DIFFRAC.EVA 4.3.0.1 software was employed. The theoretical penetration depth for XRD was calculated with the AbsorbX software using the cementite density of 7.69 g/cm³ and the Cu-K α radiation source (λ =1.54 Å).

3.3.3 TEM, STEM, and EDS

The evolution of the cementite microstructure and elemental distribution under single-pass and multi-pass wear load was investigated in detail via TEM, STEM, and EDS (Chapters 4, 5).

² XRD measurements and data evaluation were performed by B. Breitbach, Max-Planck-Institut für Eisenforschung GmbH.

For inspection by TEM and related techniques, very thin specimens are required. We prepared cross-section specimens using a lift-out technique in a Thermo Fisher Scientific Scios 2 DualBeam FIB-SEM system with a Ga⁺ ion source at 30 kV acceleration voltage. Protecting the outermost layers from the beam damage was essential since the regions of interest are adjacent to the top wear track surface. To prevent damage to the material during FIB-milling, the wear track surfaces were initially covered with a thin 2.5 µm Pt layer, which was deposited using an electron beam for the first 100 nm thickness and a faster ion beam for the remaining Pt layer. After the initial cutting with a 15 nA current, extraction with the thin needle manipulator, and mounting on the Cu grid, the specimen was further milled and polished. The beam current was 1.6 nA during the initial milling steps and was gradually decreased down to 10 pA for the polishing and cleaning step after the specimen thickness attained the required 100 nm.

The TEM and STEM analysis in this thesis was conducted in JEOL JEM-2200FS and JEOL JEM 2100PLUS microscopes operated at 200 kV acceleration voltage. Most TEM and STEM images were obtained under bright-field (BF) imaging mode. TEM images in the dark-field (DF) mode were also captured by selecting specific reflections in the selected area electron diffraction pattern with the objective aperture.

The EDS analysis of the elemental distribution of selected regions (Chapter 5) was conducted in STEM on a JEOL JEM-2200FS microscope equipped with the EX24221M1G5T detector operated at a 200 kV acceleration voltage. Although the precise atomic concentrations are difficult to evaluate due to the spurious X-rays mainly originating from the objective pole piece in the TEM, as well as due to the carbon and oxygen contamination of the specimen surface from the atmosphere, EDS provides a semi-quantitative analysis of the relative elemental differences in the studied areas. However, care was taken that all EDS measurements were performed under identical conditions. The following acquisition parameters were used for the measurement: 7.475 nA probe current, 71 min total acquisition time, and 8 min dead time. For the quantification of peaks, k-factors of 2.072, 1.1453, 1, 1.2762, 2.9773, and 2.401 were applied for C, O, Fe, Cu, Ga, and Pt, respectively. Due to the sample milling with Ga+ ions, mounting on a Cu grid, and Pt protective coating, additional gallium (~0.1 at.%), copper (~5 at.%), and platinum (~0.1 at%) signals are observed in the EDS line profiles. Fig. A4 in Appendix A demonstrates the overall spectrum from the region of interest and detected elements.

3.3.4 APT³

For the elemental distribution measurements in the topmost deformed region after the single-pass wear experiment (Chapter 4), APT was performed. The needle-like tips were milled using FEI Helios NanoLab 600 Dual Beam FIB/SEM with Ga⁺ ion source at 30 kV. In order to protect the needles extracted from the wear tracks, those regions were covered with a thin 0.5 µm Pt layer prior to milling. The current was changed from 9 nA for coarse milling to 0.23 nA, 80 pA, and 24 pA for sharpening the tip to a diameter of about 60-70 nm. The final cleaning step was executed at 5 kV and 15 pA. The APT measurements were carried out under ultrahigh vacuum in a Cameca LEAP 5000XR atom probe instrument in voltage mode (15% pulse fraction, 200 kHz pulse frequency) with a 0.5% detection rate and at a temperature of 60 K. Due to the material inhomogeneity, porosity, and residual stresses after wear tests, the tips often tend to fracture under a high electric field. The AP Suite 6.1 was used for data analysis and tip reconstruction.

The overestimation of carbon in iron carbides during APT measurements is often observed in literature and is explained by the effect of specimen temperature on iron ion detection [178,179]. At specimen temperatures below 60 K, the multiple-hit events and ion pile-up induce the detection loss for iron. The deviation from the expected carbon content is more substantial for the pulsed voltage atom probe than for the pulsed laser atom probe [180]. The difficulty in determining the absolute carbon content also arises from the mass-tocharge 24 Da carbon peak assignment, which can be either C₂⁺ or C₄²⁺ or a mixture of both [181]. We consistently distribute the peak 24 Da to half C₂⁺ and half C₄²⁺. The other peaks 6 and 6.5, 12 and 13, 18 and 18.5, 24.5 and 36 Da are assigned without ambiguity to C²⁺, C⁺, C₃²⁺, C₄²⁺ and C₃⁺, respectively. Another source for carbon overestimation is related to the crystallographic poles that affect the field evaporation [182] and result in the straight columnar structures on tip reconstructions. These structures are considered as measurement artifacts. The 1D profile and area fraction measurements were performed outside the crystallographic pole artifacts.

³ APT measurements were performed by C. Tlan, Max-Planck-Institut für Eisenforschung GmbH.

3.3.5 AES⁴

We performed AES measurements to analyze the local carbon bonding in cementite (Chapter 5). The AES has a very high lateral and depth resolution since the electrons are emitted from the top 1 nm surface layer. Therefore, AES allows for an accurate composition measurement within the wear track. The carbon spectra correspond to the KLL transitions and have distinctive shapes, depending on the chemical bonding [183–185]. These distinct shapes allow to distinguish graphitic and carbidic carbon bonds.

Auger spectra with a spot size of ~0.5 x 0.5 μ m were acquired inside and outside the wear track groove using a ULVAC-PHI 710 scanning Auger microprobe (SAM) with a spatial AES resolution of <8 nm. During these measurements, the primary beam energy was 15 kV. Sputtering with 1kV Ar⁺ ions during Zalar rotation was performed for 90, 120, and 210 min to obtain AES spectra at different depths.

3.3.6 XPS⁵

For the phase analysis of the worn cementite surface (Chapter 5), XPS spectra were recorded on the 200-wear-track array (area 1mm x 1mm, Fig. A5 in Appendix A) and undeformed surface using a PHI Quantera SXM spectrometer with an Al-K α source. The beam size was set to 100 µm. Probing a large area is advantageous because local sample inhomogeneities do not impact the results in these measurements as much as they would if a small beam size were used. In these investigations, we focus on systematic composition differences. A pass energy of 112 eV and an energy step size of 0.2 eV were employed for the spectra acquisition of the survey scan. To obtain the core level spectra of iron (Fe 2p), carbon (C 1s), and oxygen (O 1s), pass energies of 55 eV, 26 eV, and 26 eV, as well as energy step sizes of 0.05 eV, 0.025 eV, and 0.025 eV were used, respectively. In all measurements, the take-off angle was set to 45°. To perform depth profiling, 500 eV Ar⁺-ions were used to sputter the studied areas in a step-wise fashion with an overall duration of 1026 s. The sputtering rate was assumed as ~35 nm/min, leading to an overall sputtered depth of 600 nm.

⁴ AES measurements were performed by U. Hagemann, University of Duisburg-Essen.

⁵ XPS measurements and data analysis were performed by J. M. Prabhakar, Max-Planck-Institut für Eisenforschung GmbH.

We performed the peak fitting using the CasaXPS 2.3.22 software. The Shirley-type backgrounds were subtracted for all spectra. For the asymmetric metallic iron peak, the LA(1.2,4.8,3) peak shape was fitted, whereas a Gaussian (70 %) - Lorentzian (30 %) peak shape was used for the symmetric components [186]. For the Fe 2p_{3/2} spectra, the following components were fitted: Fe-metal at 706.7 eV, Fe-carbide at 707.1 eV, Fe₃O₄/FeO (Fe2+) at 708.8 eV, Fe₂O₃ (Fe3+) at 710.5 eV and Fe₂O₃-satellite at 711.6 eV. The literature on XPS characterization of iron carbides is scarce. In some studies, the binding energy for Fe-cementite was reported as 708.2 eV [187-189], whereas other works mention values similar to that of metallic Fe, i.e., 707.2-707.3 eV [190,191] due to the metallic-covalent bonding. We adjusted the position of the cementite peak to 707.1 eV based on the Fe 2p_{3/2} spectra of the undeformed cementite at the end of the sputtering period (1026 s) because the cementite iron peak is expected to be dominant in this case. This binding energy is similar to the one reported for Fe-Hägg carbide, i.e., 707.0-707.3 eV [192,193], and therefore we use a single peak for fitting both Fe-carbide compounds. The C 1s spectra were typically assigned to the carbidic C at 283.5 eV and graphitic C at 284.9 eV. Literature gives the binding energies in the range of 283.2-283.6 eV for the carbidic C peak (cementite, Hägg carbide) [188,193–196]. To account for the carbon contamination during sample preparation and storage, further C peaks were fitted into the C 1s spectra that were measured before and after the initial sputtering steps: Ca₂C at 282.0 eV, C-O at 286.2 eV, C=O at 287.4 eV, O-C=O at 288.7 eV, and CaCO₃ at 289.7 eV [189]. The O 1s spectra were fitted using the following compounds: iron oxide at 531.9 eV, FeO(OH) at 530.2 eV, CaO at 530.8 eV, and C=O/H₂O at 533.8 eV.

3.3.7 Confocal microscopy

The wear track groove measurements in this thesis (Chapters 6, 7) were conducted with a Keyence confocal microscope VK-X1000 equipped with a 405 nm laser that provides 12 nm vertical resolution and 50 nm lateral resolution at scans via a 50x lens. The confocal microscope is a useful instrument for investigating the wear track groove formation. Even though the residual penetration depth can be determined based on the three measurement segments of the microscale wear experiment, as described in section 3.2.1, confocal microscopy allows for measuring the side and front pile-up geometry and volume as well as correlating the pile-up with the residual wear track depth.

In Chapter 6, height topography measurements of wear tracks in single grains of austenitic steel (γ-Fe) were conducted to analyze the transition from indentation to plastic plowing. To account for the influence of the nanoindenter dynamics, wear tracks with and without

a holding segment (Table 3.3) were profiled along the wear direction. The wear tracks were then measured via a confocal microscope to analyze the influence of the lateral compliance on the depth curve during the transition from indentation to wear. In addition to examining the evolution of the wear track groove and the side pile-ups of 20 µm long wear tracks in the austenitic steel, the areas below and above the undeformed surface elevation were measured. We also determined the front pile-up volume by calculating the volume above the undeformed surface elevation. This front pile-up volume was analyzed for all wear tracks without holding segment in austenitic steel.

In Chapter 7, surface profiles perpendicular to the wear track in the steady-state regions were measured in aluminum, copper, and cementite to quantify the wear track width parameters and calculate scratch hardness. For each material and wear track, 20 profiles with a 1 µm spacing were determined and averaged. Thus, it is ensured that the width measurements are not affected by local height measurement artifacts of the confocal microscope. Three methods to identify the contact width were used, as detailed in the section 3.2.2.2. Afterwards, the width measures are averaged, and the hardness is calculated from wear tracks width and the corresponding normal force.

3.4. Summary of the applied techniques in the following chapters

The performed tribological experiments and employed characterization techniques in the following chapters of this thesis are summarized in the Table 3.4.

Table 3.4. Applied tribological experiments and characterization techniques.

	Chapter 4.	Chapter 5.	Chapter 6.	Chapter 7.
	Deformation and	Chemical	On the	Scratch
	phase	evolution of	commensuration	hardness at a
	transformation in	polycrystalline	of plastic	small scale:
	polycrystalline	cementite (Fe ₃ C)	plowing at the	experimental
	cementite	during single-	microscale	methods and
	(Fe₃C) during	pass sliding wear:		correlation to
	single- and	an investigation		nanoindentation
	multi-pass	by surface		hardness
	sliding wear	spectroscopy		
Tribological	Single-pass	Single-pass wear	Single-pass	Single-pass
experiments	wear, multi-pass		wear	wear,
	wear,			nanoindentation
	nanoindentation			
Characterization	SEM, EBSD,	SEM, TEM EDS,	SEM, Confocal	SEM, Confocal
techniques	TEM, XRD, APT	AES, XPS	microscopy	microscopy

4. Deformation and phase transformation in polycrystalline cementite (Fe₃C) during single- and multi-pass sliding wear⁶

4.1 Introduction

Based on the available research, it is evident that cementite influences the tribological response of steel in many ways, both positively and negatively. A better understanding of cementite deformation mechanisms during the early and late wear stages is needed for the ongoing development of wear-resistant steels. While many studies focus on the subsurface microstructure changes of rail, wheel, and bearing steels, the deformation behavior of cementite is largely controlled by the surrounding matrix phase and precipitate size in these studies. The production of bulk polycrystalline cementite by spark plasma sintering with and without the addition of stabilizing elements [29,31,197] allowed for the inspection of the cementite wear behavior while excluding the contribution of the matrix. However, the previous research on bulk polycrystalline cementite focuses on the effect of its fraction on wear resistance.

This chapter investigates cementite deformation under tribological loading. We study the microstructure evolution of sintered polycrystalline cementite by Umemoto et al. [29] in two loading cases: micrometer single-pass sliding at a contact pressure of 31 GPa and macroscale multi-pass sliding at a contact pressure of 3.3 GPa. To address cementite's limited ductility, activated slip planes at the sides of the wear groove were determined. Examining the deformed subsurface layers reveals that the dominating deformation mechanisms differ depending on the deformation depth. The comparison between micrometer single-pass and millimeter multi-pass sliding allows us to understand the onset

⁶ This chapter is based on: H. Tsybenko, C. Tian, J. Rau, B. Breitbach, P. Schreiber, C. Greiner, G. Dehm, S. Brinckmann, "Deformation and phase transformation in polycrystalline cementite (Fe₃C) during single- and multi-pass sliding wear", Acta Materialia, vol. 227, p. 117694, 2022.

of microstructure alterations of cementite and how these initial deformation stages translate to the microstructure after cyclic loading.

Although this chapter focuses on the deformation behavior of cementite, phase transformation below the contact surface and the effect of tribological loading on the local strength are analyzed as well. We report on cementite transformation into an iron carbide, namely Hägg carbide Fe_5C_{2} , and propose mechanisms of its formation. In addition, it is demonstrated how strengthening mechanisms during wear result in a significant hardness increase.

4.2 Results and Interpretation

4.2.1. Single-pass wear



4.2.1.1 Microstructure evolution and deformation mechanisms

Fig. 4.1. SEM images of the cementite surface (a) before and (b) after the single-pass wear experiment. (a) Initial sample microstructure with iron, iron oxide, and graphite inclusions that remain after spark plasma sintering. (b) Combined (of three images at the different wear track regions) image of the single-pass wear track with a black arrow showing the sliding direction (SD). White arrows mark wear features: a single crack event, plastic slip traces, wear debris, and pile-up at the wear track end. The white bracket denotes the indentation region "I".

As mentioned in section 3.1.1, the microstructure of the sintered sample consists primarily of fine-grained cementite (Fig. 4.1a). The remaining iron, iron oxide, and graphite are distributed differently. Iron is mainly present as grains of similar size as cementite. Some iron also formed finely dispersed iron oxide (white ultrafine particles on Fig. 4.1a). Graphite is partially stored in the elongated plate-like inclusions and is also present as spherical

particles (appear black on Fig. 4.1a) of the same size as iron oxides. Both iron oxide and graphite are found at cementite grain boundaries, while some are located inside cementite grains. The initial composition of the non-cementite phases was examined by EDS (Fig. A1, Appendix A). The diffraction pattern obtained from the carbon-rich particle demonstrates graphite reflections (Fig. A2 in Appendix A). The undeformed cementite grains contain few dislocations (Fig. A3 in Appendix A).

We start by inspecting the cementite surface after the single-pass wear experiment at high Hertzian pressure (31 GPa, Fig. 4.1b) [161]. In the indentation region "I" of the wear track (marked by a white bracket on Fig. 4.1b), we observe distinct slip traces and deformed graphite particles. After the transition to plastic plowing, the wear groove appears relatively smooth, homogeneous, and non-cementite inclusions are barely visible. Slip traces and wear debris are also found at the wear track edge. The front pile-up consists of moderately ductile flakes. The observed wear features thus are more typical for plastically deforming materials. Only a single crack was found at the groove edge near the indentation region. Therefore, the dominating wear mechanisms are plastic plowing and microcutting, and the plastic deformation below the contact surface is mainly due to extensive compression and shear strains.

To determine the activated slip planes in orthorhombic cementite during wear, we analyzed slip traces in the grains on the wear track edges (Fig. 4.2). To this end, SEM images and EBSD orientation maps of the same wear track region were studied. For the measured crystallographic orientation of each studied grain, possible slip planes were plotted. Afterwards, the experimentally observed slip traces were superimposed with the pole figures to determine the activated slip planes.

Among 10 studied grains at the wear track edge, (001), (010), (101), (110), and (011) slip planes were identified. The (001), (010), and (011) planes were activated in two grains each. In three grains, activated (101) planes were indexed, and in one case, slip on both (110) and (101) planes was observed. These findings are in good agreement with the previously reported slip planes of cementite: the predominantly but not uniquely found slip planes at ambient temperature deformation of cementite are (001), (010), and (100) [50,198]. Other (101), (110), and (011) planes usually become available for dislocation glide at high temperature [198], for the lamellar morphology [53], or under high rolling strains [57,58].



Fig. 4.2. An example of the slip trace analysis. (a) SEM image of the wear track edge, showing slip traces in several cementite grains. The analyzed slip traces are marked with black arrows. The white arrow denotes a sliding direction (SD). (b) EBSD orientation map with superimposed slip traces of two studied grains (black lines). (c) Constructed pole figures based on the EBSD orientation (purple and light blue in b). The black dot is the pole of identified slip plane. The red line represents the intersection of the slip plane with the top surface (the slip trace), which corresponds well with the traces from SEM images in (a).

In order to examine the microstructure evolution, we studied a wear track cross-section in TEM. Fig. 4.3a demonstrates the plastically deformed region with about 1.5 μ m thickness which has a layered structure. Below the deformed regions, pristine cementite grains (dark gray), as well as finely dispersed undeformed iron oxide and graphite inclusions (light gray on Fig. 4.3a) are observed.



Fig. 4.3. TEM and STEM overview micrographs of the wear track cross-section after a single-pass experiment. SD marks the sliding direction. (a) STEM BF image of the wear track cross-section with marked characteristic deformed regions. (b) TEM image of the nanocrystalline region (NR) with corresponding diffraction pattern. (c) TEM image of the area with the ultra-fine-grained region (UFGR), transition region (TR), and corresponding diffraction pattern.

Overall, three distinct deformation zones are resolved (Fig. 4.3a): a nanocrystalline region just below the wear track, followed by an ultra-fine-grained region, and transition region until the undeformed bulk cementite is reached at a depth of ca. 1.5 μ m. In the outermost 200-300 nm thick nanocrystalline region, the highest shear strains and strain rates promoted grain refinement inducing an average grain size as low as ~10 nm. Most of the non-cementite particles (iron oxide and graphite) were heavily deformed and are not discernible. Therefore, the resulting nanograin structure is relatively homogeneous. The nanocrystalline region is separated from the lower ultra-fine-grained region by a relatively abrupt transition. The 250 nm thick ultra-fine-grained region possesses a grain size of 100-200 nm. Cementite is severely fragmented and plastically deformed. The iron oxide and graphite particles are deformed as well but remain similar in size as for the undeformed bulk material. The lowest deformation layer is the transition region with a thickness of ~1 μ m. The cementite grains in the transition region reveal dislocation slip but are not fragmented into fine blocks, as they are in the ultra-fine-grained region.

For an overview, two diffraction patterns were obtained from the nanocrystalline region and the intersection of the ultra-fine-grained and transition regions. The diffraction pattern from the nanocrystalline region consists of multiple discontinuous rings (Fig. 4.3b) due to the nanoscale grain refinement and evolving texture. Although most reflections are assigned to cementite, iron, or iron oxide, some diffraction arcs correspond to the Hägg carbide Fe₅C₂. This phase was examined more closely in the following section. Some of the reflections would match as well to the ϵ -carbide phase Fe₂C. However, since no unique ϵ -carbide reflection (i.e., not overlapping with any of the other phases) was found, the possibility of ϵ -carbide formation is not discussed further.

Another diffraction pattern was obtained from both the transition and ultra-fine-grained regions (Fig. 4.3c). The reflections are primarily individual spots, but arcs due to the high density of dislocations are also observed. A diffuse halo in the area of the strongest reflections is due to graphite particles. We indexed the diffraction spots mainly as cementite and iron oxide, and none of the spots was assigned to Hägg carbide.



Fig. 4.4. (a) STEM BF micrograph of the transition region demonstrating plastic deformation of polycrystalline cementite. (b) Coarse slip steps (as highlighted with a bracket) are produced by the large number of dislocations passing on slip planes (marked with white arrows). (c) Slip transfer through the grain boundary (white arrow denotes the direction) and dislocation accumulation. (d) Shear bands (marked by brackets) and pinned dislocations between them. (e) Grain fragmentation into fine blocks by multiple slip events (a single block marked with white lines).

We characterize the transition region in more detail to explain the mechanisms of cementite refinement under tribological load (Fig. 4.4a). In the transition region, plasticity is predominantly accommodated by dislocation slip. High local stress concentrations cause the gliding of large amounts of dislocations on relatively few, often well separated, parallel slip planes (Fig. 4.4b). Dislocations thus form coarse slip steps with a height up to 40 nm (marked by the black bracket on Fig. 4.4b) and cut through the non-cementite particles. In Fig. 4.4c, we observe slip transfer across the grain boundary while some

residual dislocations are piling up. In some cases, deformation transfer between neighboring grains is accompanied by the locally intensified shear, which is accommodated by shear bands (Fig. 4.4d). In summary, cementite deformation in the transition region is inhomogeneous and results in grain fragmentation. Fig. 4.4e shows an onset of the fine cementite fragment formation (approximate dimensions 110 x 120 nm) by slip on the intersecting slip planes.

4.2.1.2 Hägg carbide formation

To further investigate the formation of Hägg carbide, we recorded another diffraction pattern by placing the selected area aperture in the middle of the nanocrystalline region (Fig. 4.5a, b). The majority of spots and rings were assigned to Hägg carbide, while some cementite and iron oxide reflections were also found. The objective aperture was then placed on two selected Hägg carbide reflections (221) and (112) (marked by red circles on Fig. 4.5c,d) to record the DF images produced by the diffracted beams. The resulting micrographs (Fig. 4.5c, d) demonstrate that nanometer-sized Hägg carbide crystallites are homogeneously distributed solely inside the nanocrystalline region and not in the ultra-fine-grained region. Most of these carbides are present in the middle of the nanocrystalline layer. This observation indicates that sufficiently high shear strains and nanoscale refinement are required to induce the phase transformation.



Fig. 4.5. Hägg carbide formation below contact surface. A dashed line marks the interface between the nanocrystalline region (NR) and the ultra-fine-grained region (UFGR), and a thin solid line defines the surface. (a) TEM image of the nanocrystalline and ultra-fine-grained regions and the position of the selected area aperture (white circle). (b) Diffraction pattern recorded from the nanocrystalline region demonstrating cementite, iron oxide, and Hägg carbide reflections. (c), (d) Images in DF mode from the selected Hägg carbide reflections. Red circles in the inserted diffraction pattern fragments mark the positions of the objective aperture used to obtain the respective images.


Fig. 4.6. 3D reconstructions of the APT specimens showing 33 at.% C and 0.3 at.% O isosurfaces. Columnar structures correspond to the crystallographic poles. The insets of higher magnification demonstrate the regions where carbon and oxygen isosurface area fractions were quantified. (a) Undeformed cementite grain. (b) Nanocrystalline region below the contact surface.

We conducted APT measurements in the undeformed cementite grain and the nanocrystalline region below the contact surface to record the local carbon distribution. Tip reconstructions with different carbon isosurfaces as well as 1D carbon and iron content profiles are given in Fig. A6 (Appendix A). Fig. 4.6 shows the needle reconstructions with 33 at.% C and 0.3 at.% O isosurfaces. While the exact absolute carbon contents are difficult to achieve due to several sources for carbon overestimation in APT (section 3.3.4), a relative comparison of the composition is possible.

Based on the 1D profiles (Fig. A6c, d in Appendix A), the average carbon content and the C/Fe ratios in the undeformed grain and nanocrystalline region are comparable. However, the carbon content increases locally in the deformed region (Fig. 4.6). The fraction of 33 at.% C isosurface area estimated in magnified insets in Fig. 4.6 is considerably higher in the nanocrystalline region (~13%) when compared to the undeformed cementite (~7%). In addition, the oxygen content is also higher in the nanocrystalline region, as more

0.3 at.% O isosurfaces are visible in Fig. 4.6b (~17% area in the nanocrystalline region versus ~11% area in undeformed grain). A slight increase in the average oxygen content is also evident from the 1D profiles (Appendix A).

4.2.2. Multi-pass wear

4.2.2.1 Microstructure evolution and deformation mechanisms

The multi-pass wear experiment with the contact pressure of 3.3 GPa was carried out to compare the microstructure evolution with the single-pass experiment at the contact pressure of 31 GPa. Fig. 4.7a demonstrates the heavily deformed worn surface with a large amount of wear debris. The tribolayer (darker area in Fig. 4.7b) is mainly composed of the material transferred from the sapphire tip and some iron oxide. Even on the much softer copper oxide, aluminum on the worn surface was also found after multi-pass wear with the sapphire tip [199]. The abraded particles from the removed tribolayer and repeated sliding lead to the contact fatigue, which results in the nucleation of brittle cracks at the surface (Fig. 4.7b). As a result, the loose wear debris is composed of the removed tribolayer and fractured cementite, promoting three-body abrasive wear. Outside the fractured regions, the deformed cementite surface is similar to the steady-state region of the single-pass wear track, which indicates nanocrystal formation (Fig. 4.1b). While no slip traces are observed, shallow plowing marks are visible. Other surfaces appear relatively smooth compared to the fractured regions. The non-cementite particles are not distinguishable.

We characterize the multi-pass wear track cross-section (outside the fractured areas) in TEM. The overall thickness of the plastically deformed cementite is much larger than for the single-pass wear and extends over the entire length of the TEM specimen (Fig. 4.8a). The three previously defined regions during single-pass wear are observed in the case of multi-pass wear as well. However, we find a number of distinctions between the microstructures after the two different loading conditions.



Fig. 4.7. SEM images of the cementite surface after the multi-pass sliding wear. (a) Overview of the worn surface. The white arrow shows the direction of the reciprocating sliding motion (SD). (b) Wear features after the multi-pass wear experiment (marked with black arrows): plowing marks, material transfer, and fractured cementite.

The nanocrystalline region (Fig. 4.8b) in the multi-pass case is similarly thick (200 nm) compared to the single-pass wear track (Fig. 4.3a). It is noteworthy that non-cementite particles are highly deformed, partially decomposed but still visible in some areas near the surface while absent further below the surface. The nanocrystalline region has an average grain size of about 20 nm and is gradually transitioning into the ultra-fine-grained region, as no sharp interface between the two regions is identifiable. The ultra-fine-grained region covers most of the specimen height (4 μ m). Iron oxide and graphite particles are mostly deformed and elongated in the direction of the highest in-plane shear stress. These elongated inclusions are likely the sites for crack initiation during contact fatigue(Fig. 4.7b). Some larger graphite particles are found as well. In the transition region, the grains are not distinctively fragmented by slip on a small number of parallel far-spaced slip planes, as in the single-pass case. Coarse slip steps and shear bands are not observed, and the non-cementite particles appear undeformed. Nonetheless, the density of homogeneously distributed dislocation lines and dislocation loops is high.



Fig. 4.8. STEM BF micrographs of the wear track cross-section after the multi-pass experiment with marked deformed regions. SD marks the sliding direction. (a) Overview of the deformed regions. (b) Nanocrystalline region (NR). (c) Ultra-fine-grained region (UFGR). (d) Transition region (TR).

4.2.2.2. Effect of multi-pass wear on the near-surface strengthening and Hägg carbide formation

To examine the strengthening effect of cyclic wear on surface hardness, we carried out nanoindentation tests on undeformed cementite and smooth non-fractured surface regions after the multi-pass experiment. Fig. 4.9a compares hardness as a function of the penetration depth until 1200 nm for the undeformed area as well as the smooth non-fractured area of the worn surface. The average hardness at 500 nm (H_{500nm}) was calculated using a depth range of 400-600 nm, whereas the 1000 nm hardness (H_{1000nm}) was determined by averaging the values between 900 and 1100 nm. The scatter is slightly higher in the deformed case but remains comparable to the undeformed curves. The hardness increase ΔH_{500nm} and ΔH_{1000nm} of the worn area compared to the undeformed

sample are 2.7 GPa and 2 GPa, respectively. Hence, we demonstrate a strong local increase of hardness due to strain hardening after severe deformation of cementite during tribological loading.

The XRD measurements were conducted to analyze the relation between microstructure refinement and phase transformation. The calculated X-ray penetration depth in cementite (section 3.3.2) varies from $0.9 \ \mu m$ (at $2\theta = 20^{\circ}$) to $4.6 \ \mu m (2\theta = 120^{\circ})$. In the region of the major reflections ($2\theta \sim 45^{\circ}$), the penetration depth was 2.05 μm . As shown in Fig. 4.9b for an undeformed area, cementite reflections are strong; whereas, in the worn region, the intensity decreases and peaks broaden due to grain refinement and a high dislocation density. In the deformed case, cementite peaks appear to shift to lower angles, attributed to lattice distortion and increased interplanar spacing as strain increases. Some reflections weaken in the worn case compared to the undeformed sample, while the intensity of others remains roughly similar. For instance, the strongest cementite (031) reflection ($2\theta = 44.9^{\circ}$) loses most of its intensity, whereas the (220) peak ($2\theta = 44.6^{\circ}$) remains relatively strong. These observations indicate texture development. According to the results of the Rietveld analysis [177], the average crystallite size decreased from 436±18 nm in the undeformed area to 9±1 nm after cyclic tribological loading.



Fig. 4.9. (a) Nanoindentation hardness measured on undeformed (solid lines) and worn cementite (dashed lines). The gray areas mark the depth ranges where the average hardness values were determined. (b) XRD patterns obtained from the undeformed cementite and inside the multi-pass wear track with superimposed peak positions of cementite (blue lines) and Hägg carbide (red lines). The 2θ range was selected to show the strongest experimental reflections.

In section 4.2.1.2, we relate the nanoscale grain refinement below the contact surface to the formation of Hägg carbide. When comparing experimental XRD patterns with the

superimposed peak position lines, we do not identify any Hägg carbide reflections. The intensity at the major Hägg carbide reflections ($2\theta = 43.5, 44^{\circ}$) slightly increases because of the cementite peak broadening and overlapping. This observation is consistent with our findings that demonstrate the formation of Hägg carbide in the nanocrystalline region but not in the ultra-fine-grained region (Fig. 4.5). Since the penetration depth during XRD was 0.9 µm-4.6 µm, a large portion of the XRD data stems from outside the 200 nm thick nanocrystalline region.

While inspecting the electron diffraction pattern from the nanocrystalline region and the ultra-fine-grain region of the multi-pass wear track, we observe rings attributed to Hägg carbides (Fig. 4.10). These findings are similar to those of the single-pass experiment. Other reflections are indexed as cementite and iron oxides.



Fig. 4.10. (a) Nanocrystalline region transitioning into the ultra-fine-grained region below the contact surface of the multi-pass wear track with a marked position of the selected area aperture (SAA) and (b) corresponding diffraction pattern with reflections mainly assigned to cementite, iron oxides, and Hägg carbide.

4.3 Discussion

4.3.1 Deformability of cementite during tribological loading

The deformability of cementite is generally a point of interest. The number of independent slip systems is assumed to be limited, and cross-slip is hindered. Hence, cementite is considered inherently brittle [53,55,71]. At high temperatures, activation of specific dislocation glide systems is reported in the literature [198]. Dislocation plasticity under specific loading conditions is reported [53,57,58]. Here, cementite tends to deform plastically through the activation of multiple slip systems during sliding wear (Fig. 4.2). Below the contact surface (Fig. 4.3, Fig. 4.8), plastic deformation is accommodated by several mechanisms discussed in the following section.

The increased cementite ductility is promoted by the relatively constrained volume during tribological loading. In this regard, sliding wear is similar to the other severe plastic deformation techniques, where the constrained specimen volume during processing causes a substantial increase in hydrostatic pressure, affecting the deformation behavior of the material [43,200]. During deformation under high hydrostatic pressure conditions, e.g., high pressure torsion, cementite shows notable plasticity when embedded in a matrix [15,201]. In our case, wear experiments on the polycrystalline bulk cementite also result in a local increase of hydrostatic pressure and, thus, ductility enhancement.

Another crucial factor for cementite deformability is the dynamically evolving stress-strain field as the tip is plowing through the material during sliding contact. Based on the single-asperity sliding model by Hamilton [202], the compressive stresses increase in front of the passing tip, while tensile stresses grow at the tip backside in the plane of the normal and sliding directions. Shear stresses intensify below the contact surface, whereas the exact position of the maximum normalized von Mises yield parameter depends on the friction coefficient [202]. Therefore, the deformation below the contact surface (Fig. 4.3, Fig. 4.8) primarily results from the high compressive and shear stresses.

During sliding wear, frictional heat can lead to temperature increase that can further promote cementite ductility. Several studies pointed out the drastic increase of temperature in the rail-wheel contact zone [203,204]. In the single-pass wear experiment, the wear velocity is relatively low, the local temperature rise is a rapid one-time event, and frictional heat immediately dissipates. However, for multi-pass wear track, due to a large number of strokes and a high sliding frequency of 25 Hz, frictional heat in the contact zone

potentially affects cementite deformability. Nonetheless, the relative contributions of frictional heat as well as other factors that affect the ductility of cementite require further discussion and are not central to this investigation.

4.3.2 Microstructure evolution below the contact surface

In this section, we describe the microstructure evolution of bulk polycrystalline cementite during tribological loading. Since the compression and shear stresses gradually decrease with the increasing depth, gradient microstructures are formed in both single-pass and multi-pass experiments. By analyzing the microstructures after both experiments, we define cementite deformation mechanisms depending on the loading conditions.

4.3.2.1 Single-pass wear

In the transition region, cementite grains deform predominantly through dislocation glide (Fig. 4.4). Although the overall stresses are lower in the transition region than directly below the contact surface, the local stress concentrations cause a high dislocation activity on far-spaced slip planes. The separation of activated slip planes may be a consequence of the limited number of dislocation sources inside the cementite grains, as the undeformed cementite reveals very few dislocations (Fig. A3 in Appendix A). As a result, the deformation is highly inhomogeneous and causes the formation of coarse slip steps (Fig. 4.4b), and, subsequently, grain fragmentation (Fig. 4.4e). The fragmentation of the original spherical cementite grains into the fine blocks by slip was previously reported during dry sliding of steels [15,58]. In those articles, the stress intensifies at the matrixcementite interface due to the matrix flow around the cementite particles until the cementite shear strength is reached. In the case of the polycrystalline cementite, the load is transferred from the shallow, highly deformed ultra-fine-grained layer and within the transition region during sliding wear. Inhomogeneous slip in the highly deformed grains results in dislocations pile-up and stress concentrations at the grain boundaries (Fig. 4.4c). When the transferred shear strain is sufficiently intense, shear bands form (Fig. 4.4d).

In the ultra-fine-grained region, moderate shear stresses result in the complete fragmentation of the initial cementite grains into 100-200 nm subgrains (Fig. 4.3a). Further shearing by dislocation slip is less pronounced at this grain size, and we propose that grain boundary sliding is the dominant deformation mechanism. This change of the favored deformation mechanism at different grain sizes is consistent with molecular dynamics simulations of polycrystalline cementite subjected to tensile loading by Ghaffarian et al. [56]. As the grain size decreases, dislocation glide becomes less preferred, and grain

boundary sliding accommodates plasticity instead [56]. In the work of Terashima et al. [61], bulk polycrystalline cementite with an average grain size of 0.7 µm exhibited brittle failure during room temperature compression, whereas at elevated temperatures, extensive ductility through grain boundary sliding was achieved. On the other hand, Todaka et al. [62] reported sliding of 100-200 nm cementite fragments as one of the main cementite deformation mechanisms in pearlitic steel during cold rolling. Although the matrix influences cementite deformation mechanisms in pearlitic steels, the reported findings agree with our observations: a sufficiently small grain size is required for cementite to deform by grain boundary sliding at room temperature. These small grains develop by fragmentation of the initially larger grains.

In the nanocrystalline region (Fig. 4.3b), severe deformation facilitates the further reduction of the grain size to the nanoscale. Below the contact surface, the highest shear stresses result in the accommodation of the highest strains compared to the other subsurface depths. These intense localized strains result in further grain refinement potentially through a mechanism similar to shear band formation. The refined nanoscale subgrains deform by grain boundary sliding and grain rotation, similarly to the nanostructured cementite crystallites in highly strained cold-drawn pearlite wires [205]. Since carbon tends to reduce the saturation grain size during severe plastic deformation by suppressing grain boundary sliding [206], the mechanically mixed carbon from decomposed graphite inclusions likely affects the grain size in the nanocrystalline region.

4.3.2.2 Multi-pass wear

We now discuss the microstructure alterations during multi-pass wear while considering the unraveled deformation mechanisms during single-pass wear. It is noteworthy that these wear experiments are substantially different. Regarding the loading conditions, the single-pass wear track was conducted at high contact pressure but low wear velocity, as opposed to the multi-pass test, in which moderate contact pressures and a high wear velocity were employed.

The principal difference between both experiments is the number of wear passes and the sliding direction. We executed the single-pass test as a single asperity unidirectional sliding contact. Hence, there is an analogy to the contact model of Hamilton [202]. However, the multi-pass wear track was produced by cyclic reciprocating sliding with a large counterbody, resulting in multiple asperity contact. The friction coefficient and the corresponding material response below the contact surface differ from the single-pass wear and change with each tip stroke. The material transfer from the tip to the contact

surface affects the wear response as well. Moreover, contact fatigue is accompanied by abrasive debris formation (Fig. 4.7), leading to the three-body contact regime. Therefore, during multi-pass wear, the stress-strain state below the contact surface and the microstructure evolution are dynamically evolving and much more complex than in the single-pass experiment. Overall, the single-pass wear experiment provides better insight into the cementite deformation mechanisms based on the loading state, whereas the multi-pass experiment resembles microstructure evolution in real contact.

Despite the differences in loading conditions, wear directions, and tip materials, the comparison of the subsurface microstructures after both sliding tests reveals the same deformation mechanisms that accommodate plasticity. However, their relative contributions to the microstructure alterations are different. In the multipass experiment, the transition region is located further from the contact surface compared to the single-pass case. As the transition region is located lower and the applied load is lower than for the single-pass wear, the stress intensities are generally lower, and the stress field is more homogeneous than in the transition region of the single-pass wear track. Consequently, the dislocation activity is more homogeneous, and the slip steps and shear bands are not as pronounced (Fig. 4.8d).

The plastic deformation is primarily accommodated in the ultra-fine-grained region (Fig. 4.8c), which formed after the original cementite grains underwent fragmentation by slip during the first cycles of multi-pass wear. Due to the reciprocating motion and a large number of cycles, the in-plane deformation below the surface is different from the single-pass wear. The effect of in-plane stresses is particularly evident from the orientation of highly deformed non-cementite particles, which are elongated in the multi-stroke experiment.

In the nanocrystalline region (Fig. 4.8b), the grains appear equiaxed and nearly spherical, indicating grain rotation and grain boundary sliding. However, the plastic deformation in the nanocrystalline region of the multi-pass wear is not severe enough to promote the complete decomposition of non-cementite inclusions and their mechanical mixing with cementite. The combined effect of higher wear velocity, lower contact pressure, and presumably higher local temperature is the reason for the slightly larger saturation grain size in the nanocrystalline region and its smaller thickness when compared to the single-pass wear track.

4.3.3 Strain hardening and softening during sliding wear of cementite

The hardness measurements on the undeformed and worn surfaces provide an estimate of strain hardening during multi-pass wear (Fig. 4.9a). Please note that the hardness measurements of individual deformed regions in cross-section are not reasonable, as these regions are insufficiently thick to accommodate the complete plastic zone of a nanoindent at a significant depth.

Since the hardness after the wear experiment was dominated by the ultra-fine-grained region, the main possible strengthening mechanisms obstructing dislocation plasticity are grain boundaries (Hall-Petch mechanism) and strain hardening (Taylor hardening). Since nanoindentation was performed outside fractured areas of the worn surface, we presume that deformation mechanisms are still active in the nanocrystalline and ultra-fine-grained regions. Nonetheless, we cannot exclude the influence of cracks on the resulting hardness of the worn areas. We expect grain boundary sliding and grain rotation, associated with strain softening, as the dominant deformation mechanisms in the nanocrystalline and ultra-fine-grained regions. In addition, shear band formation in response to the critical local shear stresses leads to local strain softening. However, shear bands were not observed in the ultra-fine-grained region of the multi-pass wear track (e.g., Fig. 4.8c).

The interplay of strengthening and softening results in the H_{500nm} increase by 17% (2.7 GPa) compared to the undeformed cementite. Hence, the strengthening effects dominate the softening effects.

4.3.4 Hägg carbide formation

Hägg carbide (Fe_5C_2 or $Fe_{2.2}C$) is a transition iron carbide that forms during the last tempering stages of the high-carbon martensite and before an equilibrium mixture of iron and cementite is reached [73]. Among the transition carbides that occur during martensite tempering, Hägg carbides are the most stable and can exist in equilibrium with cementite at high carbon concentrations in the shape of microsyntactically intergrown thin layers [46,75,76]. In the Fischer-Tropsch synthesis, the Hägg carbide is related to the active catalyst phase of the iron-based reaction [207].

This is the first time Hägg carbides were observed after sliding wear experiments on cementite. To explain the formation of Hägg carbide, it is essential to understand the conditions and mechanisms of its precipitation. Several synthesis processes were previously reported. For instance, during the carburization of iron in $CO-H_2-H_2O-H_2S$

gases at 500 °C for carbon activities exceeding a_c =150 [208], Hägg carbides grow on top of cementite [74]. According to Barinov et al. [78], Hägg carbide formation proceeded after the complete synthesis of cementite during low-temperature ball milling of iron powders in a liquid hydrocarbons medium. The authors argued that the process of less stable highcarbon carbides (i.e., Hägg) transforming into the more stable cementite with less carbon is thus reversible. Another method for Hägg carbide mechanosynthesis involves milling iron and graphite powders in a nitrogen atmosphere [77]. During earlier milling stages, an increase in cementite area fraction was recorded, whereas at extended milling times, the cementite fraction decreased, and Hägg carbide and an ε -carbide fraction increased simultaneously. Higher ball-to-powder ratios and nanoscale refinement accelerated the transformation.

The reported data thus suggests several criteria that induce Hägg carbide formation. Carbon gradients are introduced during the ball milling with carbon-containing components and carburization processes with high carbon activities. The small octahedral interstices in cementite are not favorable for occupation by excess carbon atoms [46] when the stochiometric 25 at.% C concentration is exceeded. Hence, higher carbon concentrations provide a driving force for precipitation. Since the available literature indicates a direct conversion between the two carbides, cementite can be considered a precursor for transformation into the Hägg carbide (and vice versa). Other factors, such as high mechanical energy introduced during mechanosynthesis, nanoscale refinement, and temperature increase during carburization, greatly improve the transformation kinetics. In this investigation, during the single-pass and multi-pass sliding wear experiments on cementite, grain refinement, high mechanical energy supplied through friction, wear, and presumably a frictional temperature increase are expected to assist the phase transformation into Hägg carbides. However, the source of the excess carbon in the deformed cementite microstructure is addressed in the following.

We propose two possible sources of excess carbon. One potential source is related to the remaining finely dispersed graphite in the sintered polycrystalline cementite sample (section 2.1, Fig. 4.1a). Shearing of the non-cementite particles by a high dislocation activity in a neighboring cementite grain was observed in the transition region of the single-pass wear track (Fig. 4.4b). In the regions of the highest localized strains, i.e., nanocrystalline region or shear bands, severe shear strains lead to the further decomposition of iron oxide and graphite particles that are subsequently mechanically mixed with the surrounding cementite matrix. In the case of the single-pass wear track, we observe the complete decomposition of non-cementite inclusions in the nanocrystalline

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region (Fig. 4.3a). In the multi-pass wear track, the decomposition in the nanocrystalline region is limited (Fig. 4.8b). However, in the area without distinct non-cementite particles of the multi-pass wear track, the diffraction pattern also shows Hägg carbide reflections (Fig. 4.10).

On the one hand, the thorough mixing of graphite with cementite is expected to increase the overall carbon content in the nanocrystalline region. However, according to APT results (Fig. 4.6, Fig. A6 in Appendix A), the average carbon content is almost identical in undeformed cementite grain and the nanocrystalline region. The local redistribution of carbon is evident from the 3D sample reconstructions. On the other hand, it is possible that simultaneous mixing of iron oxide and graphite with cementite does not substantially affect the overall iron to carbon ratio, but local carbon enrichment can occur. This explanation is supported by oxygen content increase in APT of the nanocrystalline region and FeO reflections on the diffraction patterns (Fig. 4.3b, Fig. 4.5b, Fig. 4.10b).

An alternative source for carbon can arise from oxidation due to tribological loading and frictional heating in the contact zone. The phenomenon of tribo-oxidation was extensively studied in the past and generally occurs in unlubricated steels and alloys [209,210]. Cementite tends to corrode at high temperatures and oxidizes naturally at room temperature, producing amorphous Fe-based oxides and Fe_2O_3 and Fe_3O_4 , and other common metallic iron oxides [211]. The carbide oxidation reactions can be accompanied by the formation of CO_2 [212,213], which provides a source of excess carbon for the transformation analogous to the carburization process. Therefore, we suggest that tribo-oxidation can potentially lead to the release of Fe from cementite with Fe forming oxides in the air. Simultaneously carbon enriches the remaining cementite or forms CO_2 , both acting as sources for the Hägg carbide formation.

Wear velocity and the associated frictional temperature increase are among the main factors that can accelerate tribo-oxidation. The sliding conditions are not favorable for oxidation in the single-pass wear track since a single stroke at low sliding speed was performed. However, even in these conditions, a slight increase of oxygen content in the nanocrystalline region is observed according to APT results (Fig. 4.6). This oxygen increase could occur due to the decomposition of the iron oxide FeO particles found in the initial microstructure (section 3.1.1, Fig. 4.1a). Nonetheless, the iron content did not increase similarly in the deformed region. As mentioned above, the constant iron content may be due to the simultaneous decomposition of graphite and iron oxide, leading to the same overall iron to carbon ratio as in the undeformed cementite. However, the most inner

reflections of the diffraction pattern from the nanocrystalline region of the single-pass wear track correspond to Fe_2O_{3} , and Fe_3O_4 oxides (Fig. 4.5b), which were not detected in the undeformed sample. Therefore, the alternative carbon source based on tribo-oxidation of cementite is also plausible.

When excess carbon is introduced to the microstructure, it is mixed with the surrounding cementite and assisted by microstructure refinement. The deformation-driven cementite fragmentation and high defect density lead to an increase of the free energy associated with the formation of new interfaces [214,215]. This free energy rise leads to increased carbon solubility and allows local supersaturation with carbon atoms. A shift of the XRD peaks from the ultra-fine-grained region to lower angles due to the uniform lattice straining thus is explained by an increase of the carbon content stored within cementite lattice (Fig. 4.9b). Moreover, the formation of new grain boundaries would further facilitate the redistribution of the excess carbon atoms since the diffusion coefficients at grain boundaries are higher than in bulk [216]. The resulting system would be thermodynamically unstable and can lead to the formation of the Hägg carbide.

The proposed mechanisms for enhanced carbon mobility in the pearlitic steel in the vicinity of dislocations are based on the difference between the binding energies of carbon in cementite and carbon at a dislocation core in ferrite [181,217,218]. The binding energy of carbon to dislocations in cementite was not previously calculated. Therefore, these mechanisms are not directly applicable to polycrystalline cementite.

The kinetics of cementite transformation into Hägg carbide is also related to the crystal structure similarities of the two phases. Both structures are often represented by layers of trigonal prisms from iron atoms with carbon atoms located inside the prismatic sites. The individual arrangement of prisms defines the carbide structure and is the basis for the concept of chemical twinning, according to which Hägg carbide can transform into cementite [219,220]. Since the formation of the Hägg carbide occurred solely in the nanocrystalline region with the highest shear strains, we presume that the inverse phase transformation is promoted by straining the carbon-saturated cementite lattice and its subsequent shearing. As a result, a single-pass sliding experiment with high contact pressures is sufficient for the mechanosynthesis of Hägg carbide, as opposed to the previously reported synthesis by ball milling [77,78], which requires a longer duration and long-term diffusion-driven carburization processes [74].

4.4 Conclusion

We systematically analyzed deformation and chemical evolution in bulk polycrystalline cementite during single-pass and reciprocating multi-pass sliding. We revealed the deformation mechanisms in cementite during wear by means of EBSD and TEM and measured the nanoindentation hardness. The formation of Hägg carbides was reported and further investigated by TEM, XRD, and APT. In summary, the main findings are:

- During sliding wear, cementite deforms plastically through slip activation on (001), (010), (101), (110), and (011) planes. The improved ductility is due to the volume confinement during wear. The stress-strain state due to shear and compression results in moderate plastic deformation and a potential temperature increase in the contact region.
- The cross-sections of single-pass and multi-pass wear tracks reveal gradient deformed microstructures classified into three layers: a top nanocrystalline region, followed by an ultra-fine-grained region, and an extended transition region before the undeformed matrix is reached. Dislocation slip and shear band formation are observed in the transition region, indicating that dislocation-based plasticity is the origin of grain refinement down to 10-20 nm in the nanocrystalline region. We assume that below the contact surface (nanocrystalline region and ultra-finegrained region), the highest shear strains are mainly accommodated by grain boundary sliding and grain rotation. These mechanisms lead to the diffraction arcs (preferred orientations) observed in electron diffraction patterns.
- The multi-pass experiment results in the three-body abrasive wear and brittle fatigue crack formation. Outside the fractured regions, the wear track cross-section is characterized by different deformed layers thicknesses compared to single-pass wear. The stress state is more homogeneous in the transition region of the multipass wear track, leading to homogeneously distributed dislocations with no pronounced slip steps or shear band formation. The ultra-fine-grained region is 4 µm, much thicker than in the single-pass wear track with ~1 µm, whereas the nanocrystalline region has a similar thickness. The interplay of strengthening and softening effects upon deformation results in the nanoindentation hardness increase by up to 17% (2.7 GPa).

We detect the formation of Hägg carbides in the outermost nanocrystalline regions of both wear tracks. The nanocrystalline region of the single-passed wear track has locally increased carbon content and a slight but noticeable increase in oxygen. However, the overall carbon content, as well as the carbon to iron ratio, remain similar to the undeformed cementite grain. It is proposed that the excess carbon promotes cementite transformation into Hägg carbide by inducing local carbon enrichment in the cementite phase. This excess carbon may arise due to the deformation-driven decomposition of the finely dispersed graphite particles present in the original microstructure or the tribo-oxidation of cementite, leading to the loss of iron. Other factors, such as high mechanical energy, free energy changes, nanoscale refinement, potential temperature increase, and crystal structure similarities, support the phase transformation.

5. Chemical evolution of polycrystalline cementite (Fe₃C) during single-pass sliding wear: an investigation by surface spectroscopy⁷

5.1 Introduction

It is essential to relate the wear performance of cementite to its underlying deformation behavior and chemical evolution during tribological loading. In the previous chapter, the deformation mechanisms of bulk cementite during single-and multi-pass sliding wear were inspected. The wear experiments led to severe plastic deformation in the contact region. The effect of tribological loading on chemical evolution was marginally addressed. In particular, the Hägg carbide formation in the outermost layer of the wear track was detected. The formation of Hägg carbides in the contact region indicates the existence of carbon gradients, which provide a driving force for precipitation. Those initial results suggested two possible explanations for the excess carbon that promotes phase transformation: decomposition of graphite particles and oxidation of cementite during wear [221]. More evidence is required to provide conclusive support for one of the suggested mechanisms.

This chapter focuses on the chemical evolution of sintered polycrystalline cementite [29] during single-pass sliding wear. We employ EDS, AES, and XPS to analyze the elemental and phase composition of the deformed layers of the sample as well as of the undeformed regions. By combining these surface spectroscopy techniques, we aim to relate the deformation-related microstructure alterations to the qualitative and semi-quantitative differences in the elemental and phase distributions. Based on the results of this chapter, we validate the proposed sources for carbon enrichment in the outermost deformed region and determine feasible mechanisms for the cementite to Hägg carbide phase transformation.

⁷ This chapter is based on: H. Tsybenko, M. Prabhakar, M. Rohwerder, G. Dehm, S. Brinckmann, "Chemical evolution of polycrystalline cementite (Fe₃C) during single-pass sliding wear: an investigation by surface spectroscopy", unpublished.

5.2 Results



5.2.1 EDS analysis of the deformed layers after wear

Fig. 5.1. SEM image of the cementite surface after the microscale sliding wear experiment (combination of two images). Due to sample fabrication, non-cementite inclusions (iron, graphite, and wüstite) exist, which are marked. The white arrow shows the sliding direction (SD).

Fig. 5.1 shows the wear track groove after the microscale sliding wear experiment. The sample is chemically inhomogeneous as it contains small fractions of iron (Fe), iron oxide (FeO, wüstite) according to XRD analysis, and remnant graphite after spark plasma sintering, as concluded based on the EDS measurements (Appendix A). Graphite is distributed in spherical and plate-like inclusions (black features in Fig. 5.1). The same black features are also assigned to the porosity that remains after the sample preparation. The remaining iron is located in relatively large grains that are similar to cementite. Small spherical particles consist of iron oxide FeO (light gray in Fig. 5.1). Inside the wear track groove, the non-cementite particles are difficult to distinguish, and the surface appears smooth.

We start the chemical investigation by examining the local elemental distribution in the wear-track cross-section via EDS (Fig. 5.2). Below the contact surface (Fig. 5.2a), the microstructure is severely deformed and is divided into three distinct layers, as discussed in the Chapter 4: a nanocrystalline region right below the wear track, an ultra-fine-grained region, and a transition region towards the bulk virgin material.



Fig. 5.2. EDS measurements of the wear track cross-section. (a) STEM bright-field (BF) image of the wear track cross-section after a single-pass experiment with marked characteristic deformed regions [221]: nanocrystalline region (NR), ultra-fine-grained region (UFGR), transition region (TR). The blue dotted line marks the location of the elemental profile line in (b). (b) Elemental profile line showing atomic concentrations of iron, oxygen, and carbon. The dotted line highlights the approximate boundary between the nanocrystalline region and the ultra-fine-grained region. (c-g) EDS mappings for the region in (a). The vertical carbon-depleted and iron-enriched regions are caused by FIB milling artifacts, i.e., curtaining, and are already visible in the bright-field STEM image (a). The horizontal white dashed lines mark the approximate boundaries between the characteristic regions as highlighted in (a).

Apart from the cementite grains, we observe the finely dispersed graphite and iron oxide particles (light gray particles in Fig. 5.2a) in the ultra-fine-grained and transition regions. These particles are of similar size and are distinguished based on the EDS elemental mappings (Fig. 5.2 c-g). While iron oxide inclusions are carbon-deficient compared to the surrounded cementite, graphite particles have an abundance of carbon (Fig. 5.2f). Graphite particles also contain some oxygen, as evident from Fig. 5.2g. In the outermost nanocrystalline region, the elemental distribution is relatively homogeneous, and the individual non-cementite inclusions are barely visible, which is caused by deformation-driven decomposition due to the severe shear strains and high strain rates. We also observe slightly higher oxygen and carbon concentrations in the nanocrystalline region compared to the other deformed regions (Fig 5.2f,g).

The relative differences in atomic concentrations are also evident from the line profile across the nanocrystalline and ultra-fine grain regions in Fig. 5.2b. This line profile was obtained from the same region where Hägg carbide formation was previously observed [221]. Right below the wear track (20-80 nm from the contact surface), the atomic fraction of iron is the highest (67 at.%) and decreases gradually with the increasing distance from the contact surface to 61 at.%. In the same depth range, the carbon concentration increases from 23 at.% to 31 at.%, while oxygen concentration decreases from 4.7 at.% to 3.5 at.%. As the distance from the contact surface increases further (80-240 nm), the atomic concentrations fluctuate around constant values (61.6 at.% Fe, 30.1 at.% C, and 3.7 at.% O) with the local changes not exceeding 4 at.%. These fluctuations indicate that the mechanical mixing in the nanocrystalline region did not result in a homogeneous elemental distribution. In the ultra-fine grain region, local fluctuations also occur. However, the overall trends of the atomic concentrations are changed. The atomic concentration of iron increases, whereas oxygen and carbon concentrations decrease. Another line profile across the nanocrystalline and ultra-fine grain region about 330 nm to the right from the profile on Fig. 5.2b was recorded, and that line confirms these concentration trends (Fig. A7). In the undeformed cementite grains, the average atomic concentrations of iron, carbon, and oxygen concentration are 76.4 at.%, 16.3 at.%, and 0.8 at.%, respectively, as measured by EDS.



5.2.2 AES analysis of carbon bonding outside and inside in wear track

Fig. 5.3. Auger electron spectra acquired from the (a) undeformed cementite grain and (b) wear track surface at three increments of Ar⁺ sputtering 90, 120, and 210 min. The positions of the carbon, oxygen, and iron peaks are marked.

Fig. 5.3 demonstrates the derivative Auger spectra obtained from the undeformed cementite grain and the wear track surface. The carbon spectra correspond to the KLL transitions and have distinctive shapes, depending on the chemical bonding [183–185]. The distinctive shape allows to distinguish between carbides (carbon-metal bonding) and graphite (carbon-carbon bonding). The carbon spectra recorded at the first two sputtering steps from the undeformed cementite grain (Fig. 5.3a) correspond to the combination of the two bonding types. This observation indicates the presence of carbides and graphite; the latter exists due to the remnant surface contamination or due to graphite particles in the region. After 210 min of sputtering, a typical carbon-metal bonding line-shape is revealed. Inside the wear track, the Auger spectra for carbon are composed of the two carbon line-shapes after all sputtering steps: this detail confirms the presence of graphite (in addition to carbides) in the deformed region. It is noteworthy that iron oxide and graphite are lighter components with lower binding energy and therefore are selectively etched compared to cementite during the sputtering process [222], affecting the measurement results (Fig. A8 in Appendix A).

5.2.3 XPS investigation of the phase composition

To examine the phase composition in the deformed layers, we perform a comparative analysis of the XPS depth profiles in the undeformed cementite as well as in the wear array area. Fig. 5.4 presents the Fe $2p_{3/2}$ and C 1s spectra obtained after one of the initial

sputtering steps (126s, 70 nm depth). At this sputtering step, the component peaks are a combination of the surface contamination layer and the sample bulk.



Fig. 5.4. XPS spectra recorded after 126 s of sputtering (~70 nm depth) from the undeformed cementite and the wear track array. (a) Fe $2p_{3/2}$ spectra with deconvoluted Fe-metal, Fe-carbide, Fe₃O₄/FeO, Fe₂O₃, and Fe₂O₃-satellite peaks. (b) C 1s spectra with deconvoluted C-carbide, C-graphite, C-O, C=O, O-C=O, and CaCO₃ peaks.

The Fe $2p_{3/2}$ spectra are composed of five peaks (Fig. 5.4a): Fe-metal, Fe-carbide, Fe₃O₄/FeO, Fe₂O₃, and Fe₂O₃-satellite. Due to the oxidation of the metallic iron and FeO in the atmosphere, additional peaks of Fe₂O₃ and Fe₂O₃-satellite are expected. Since the difference between the binding energies of the overlapping Fe-metal and Fe-carbide is small (~0.4 eV), the spectra decomposition leads to ambiguous results at ~707 eV. Therefore, we refer to the sum of the Fe-metal and Fe-carbide concentrations in the quantitative phase analysis. We deconvoluted the C 1s spectra using the following compounds: C-carbide (cementite, Hägg carbide), C-graphite, C-O, C=O, O-C=O, and CaCO₃ peaks. While CaCO₃ is a component of the surface contamination layer, C-graphite, C-O, C=O and O-C=O are also present in the bulk sample, as was evident from the previously discussed EDS observations (Fig. 5.2g). The difference in the binding energies between the C-carbide C-graphite is rather large (~1.4 eV), allowing for the adequate quantification of the individual fractions. For convenience, we refer to the sum of the C-O, C=O, O-C=O, and CaCO₃ fractions as other C-compounds during phase composition analysis.



Fig. 5.5. (a) XPS depth profiles for undeformed cementite and wear track array. (b) C-carbide, C-graphite, and other C-compounds at.% fractions throughout XPS depth profile (c) Fe-metal/carbide and Fe-oxide at.% fractions throughout XPS depth profile.

The XPS elemental depth profiles (Fig. 5.5a) show similar trends for undeformed cementite and deformed wear track arrays. With extended sputtering periods and higher depth, the surface contamination is gradually removed, revealing the composition below the surface. The atomic concentration of iron rapidly increases until 300 s (175 nm) but does not demonstrate a drastic change after further sputtering, increasing gradually by an additional 10 at.%. The fraction of carbon is initially high (70 at.%) due to surface contamination, which is dissociated during the first two sputtering periods between 0 s and 36 s (0-21 nm). At the higher sputtering depth at 36-126 s (21-74 nm), there is a drop in C at.%, followed by a further increase to a constant value of ~38 at.%. The oxygen concentration initially increases from ~26 at.% at the surface to more than 45 at.% at 36-66 s (21-39 nm) and then gradually decreases to less than 8 at.% at the end of sputtering. The gradual decrease of oxygen content is related to the presence of plate-like pores that can exceed 1 µm in length (Fig. 5.1) and affect the measured composition throughout the entire depth profile (0-600 nm). The overall carbon and oxygen trends imply that the top contamination layer (0-36 s, 0-21 nm) is mainly formed by the carbon/oxygen-saturated compounds, whereas a film of iron oxide mixtures exists at higher depths. A tiny calcium fraction is detected up to ~500 s (290 nm) and is associated with Ca₂C, CaCO₃, CaO, and Ca(OH)₂ compounds [189]. Calcium might originate from the surface preparation slurry and reside in sample pores at the surface.

There are, however, several discrepancies when comparing the depth profiles from the undeformed and the wear track region (Fig. 5.5a). On the one hand, the iron

concentrations are nearly the same for the undeformed and deformed regions during the first sputtering steps. On the other hand, starting from 126 s (74 nm), the iron fraction in the deformed region is consistently 3.3 at.% lower than that in the undeformed region. Additionally, the oxygen concentrations show an opposite trend: in the 6-126s range (3.5-74 nm), the O at.% is up to 5.5 at% lower in the wear track array, whereas it is higher than the O fraction in the undeformed region by ~2.3 at.% at all subsequent sputtering steps. The carbon concentrations are also higher in the deformed case, with the highest difference of ~6 at.% between 36 and 126s (21-74 nm). Although the calcium fraction is smaller in the wear track array region, it can still be detected after a bit longer sputtering in the deformed region than in the undeformed region.

By comparing the atomic fractions of carbon and iron assigned to specific compounds, we examine the phase composition differences in more detail (Fig. 5.5b, c). After the initial maximum at the surface level, C-graphite rapidly decreases and does not significantly change after 126 s (74 nm, Fig. 5.5b). The C at.% in graphitic carbon is similar in both regions through the entire depth profile (Fig. 5.5b), except for the initial sputtering steps, after which C-graphite is smaller in the deformed region (max. difference ~13 at.% at 66 s). The same is true for the carbon in other compounds (Ca₂C, C-O, C=O, O-C=O, and CaCO₃), whereas the maximum difference does not exceed 2 at.%. On the contrary, the C at.% in the carbide phase is consistently higher in the wear track array up to 246 s (144 nm). The C-carbide fraction significantly increases between 36 and 246s (21-144 nm) and continues to increase slowly with further sputtering (Fig. 5.5b). The Fe-metal/carbide and Fe-oxide fractions are generally smaller in the wear track array, with the exception of Fe-metal/carbide concentration being slightly higher in the deformed region up to 66 s (39 nm, Fig. 5.5c). The initial Fe-oxide peak reaches its maximum at 36-66 s (21-39 nm) and then decreases to a nearly constant level at ~126 s (74 nm).

5.3 Discussion

5.3.1 Elemental and phase distribution after wear

Due to tribological loading, the non-cementite inclusions in the most severely deformed regions undergo decomposition and mechanical mixing with the cementite matrix, as evident from the EDS observations (Fig. 5.2). As observed in the Chapter 4, the intense localized strains in the nanocrystalline region lead to severe plastic deformation and grain refinement, which resembles the formation of a shear band and promotes the mechanical mixing of phases by shear transfer [223]. However, the fluctuations on the EDS line profiles

(Fig. 5.2b, Fig. A7b) indicate that deformation due to single-pass wear is not sufficient to cause the complete homogenization because local gradients in iron, carbon, and oxygen concentrations still exist. Please note, however, that single-pass wear is sufficient for the formation of Hägg carbides, as proven previously by selected electron diffraction.

Due to the mechanical mixing in the nanocrystalline and ultra-fine-grained regions, the elemental distribution in these regions is very different from the bulk cementite. According to the EDS results, right below the contact surface, the iron fraction is high (Fig. 5.2b, Fig. A7b), which does not align with the present XPS measurements (Fig. 5.5a). Since the local changes are averaged in the XPS results over a region of 100 µm diameter, we presume that the iron increase below the contact surface is attributed to the presence of an iron grain near the surface in the EDS image. We also observe in EDS a more homogenized elemental composition in the nanocrystalline region. In contrast, the elemental distribution in the ultra-fine-grained region gradually transitions towards the atomic concentrations in the bulk cementite (Fig. 5.2b, Fig. A7b).

The depth profiling in XPS reveals similar trends in elemental distribution for the undeformed and deformed regions. However, the carbon and oxygen fractions are higher in the deformed region than in the undeformed region after the first sputtering steps, and calcium is detected after longer sputtering periods. This finding is potentially related to the intermixing of the surface contamination layer and non-cementite precipitates containing carbon, oxygen, and calcium compounds with the bulk material. Another possible explanation of higher C and O fractions in the deformed region is that the measurement of the elemental distribution by XPS is partially affected by the wear-induced surface roughness that potentially prevents the uniform sputtering. Nonetheless, a substantial amount of the other carbon compounds (Ca₂C, C-O, C=O, O-C=O, and CaCO₃) is removed by 126 s of sputtering (74 nm).

5.3.2 Analysis of carbon sources for Hägg carbide formation

The Chapter 4 confirmed the formation of the Hägg carbide at the expense of cementite in the nanocrystalline region. Two mechanisms of excess carbon formation were proposed that provide the driving force for phase transformation. One way of promoting the local carbon enrichment arises from the decomposition of non-cementite inclusions that remain after sintering, i.e., the dissolution of finely dispersed graphite particles. Another scenario is based on cementite tribo-oxidation, accompanied by the loss of iron and the simultaneous relative increase in carbon, which then is available for transformation [221]. According to the previous APT measurements, a higher fraction of carbon-saturated clusters and a higher oxygen content are found in the nanocrystalline region compared to the undeformed cementite grain. Nonetheless, the average C/Fe ratio was nearly the same in both cases.

The EDS results from the same region and depth range in which Hägg carbides were detected previously (80-240 nm) demonstrate local fluctuations of 4 at.% consistent with the formation of carbon-saturated clusters. The average carbon and oxygen content was higher in the deformed than in the undeformed area. Moreover, the carbon fraction remains as high in the outer part of the ultra-fine-grained region as in the nanocrystalline region. However, the Hägg carbide formation was reported only in the nanocrystalline region. These observations emphasize the crucial role that severe shear strains play in the phase transformation to Hägg carbides.

The analysis of the cementite-Hägg carbide transformation based on XPS data is complicated because both phases have the same bonding and, consequently, the same binding energy of carbon in both carbides. Additionally, small differences between the binding energies of Fe-metal and Fe-carbide (section 3.3.6) are an obstacle to clear peak separation. Nonetheless, the comparison of carbon fractions assigned to the carbide phase (Fig. 5.5b) demonstrates a substantial increase in the C-carbide concentration in the wear track array up to 246 s (144 nm). The average difference is 4.5 at.% at 0s-186s (0-109 nm) and corresponds to the expected difference between stoichiometric cementite and Hägg carbide (3.6-6.25 at.%).

To better examine the possible carbon sources of Hägg carbide formation, we analyze the ratios of C-graphite and C-carbide fractions as well as Fe-oxide and Fe-metal/carbide fractions (Fig. 5.6) in those regions in which a higher C-carbide concentration was observed in the wear track array (Fig. 5.5b). We plot the corresponding ratios for the undeformed region and compare them to those in the wear track array. Although the ratios are affected by the surface contamination during the first sputtering steps, their overall trends reveal the excess carbon source (Fig. 5.6).

The decomposition of the remaining graphitic carbon in the sample would lead to a lower C-graphite content and a higher C-carbide fraction. As such, a C-graphite/C-carbide ratio would be lower in the deformed region than in the undeformed region. This evolution is indeed observed: the ratios of C-graphite and C-carbide fractions are lower for the wear track array. Although the decrease of C-graphite/C-carbide in the wear track array is also partially due to the removal of the surface carbon layer (until 126s, 74 nm), the small

deviation between the carbon ratio curves remains until 186s (109 nm), whereas the iron ratios coincide already after 126s (74 nm). Therefore, we assume that the lower ratios of C-graphite and C-carbide fractions are attributed to the formation of carbidic bonds of Hägg carbide and the simultaneous decrease of graphitic carbon bonds in the deformed region. Thus, the graphite decomposition resulting in carbon oversaturation and Hägg carbide formation is supported by the XPS measurements. Nonetheless, the presence of iron carbides and graphite in the deformed region indicates that the released carbon from graphite did not fully transform (see AES and XPS measurements).

The other source of carbon excess would be the tribooxidation of cementite. In this case, the Fe-oxide fraction would increase, whereas the Fe-metal/carbide fraction would simultaneously decrease. This iron redistribution would lead to a higher ratio between Fe-oxide and Fe-metal/carbide in the wear track compared to the undeformed region. This evolution is not observed in the present experiments. According to Fig. 5.6, the ratio between Fe-oxide and Fe-metal/carbide is lower in the deformed case, which indicates the removal of the surface iron oxide layer and not the formation of more iron-oxygen bonds.



Fig. 5.6. The ratios of atomic concentrations in (a) carbon and (b) iron compounds in undeformed cementite and wear track array.

5.4 Conclusion

The surface spectroscopy measurements of sample composition before and after microscale wear experiments on polycrystalline cementite reveal chemical changes due to tribological loading. The following conclusions are drawn from this chapter:

- Severe plastic deformation during tribological loading induces decomposition of non-cementite particles and subsequent mechanical mixing with the cementite matrix by shear transfer. The mechanical mixing is especially pronounced in the topmost deformed region (nanocrystalline region); however, it does not lead to a fully homogeneous elemental distribution. Mechanical mixing is not pronounced in the lower deformed regions, although the non-cementite particles are deformed.
- Although the elemental distribution in the deformed region may differ locally, the average atomic concentrations in the undeformed and deformed regions are similar. In the region covered by a wear track array, the carbon and oxygen surface contamination and iron oxide layer are partially removed and mixed with the bulk material compared to the undeformed region.
- The previously observed cementite-Hägg carbide transformation occurs in the region with an increased fraction of carbon. Comparing the iron and carbon compounds ratios reveals that graphite decomposition is responsible for the excess carbon formation in the nanocrystalline region. On the other hand, the effect of cementite oxidation on Hägg carbide formation is negligible.

6. On the commensuration of plastic plowing at the microscale⁸

6.1 Introduction

There is little systematic examination of the very first stage of wear, i.e. transition from stationary to sliding contact. Several experimental studies have reported a rapid initial depth increase during the transition from indentation to wear after the beginning of the lateral movement [37,122,135,137]. The penetration depth decreases subsequently into the steady-state regime, which depends on the loading and material configuration and which has much smaller fluctuations.

The dependence of the initial depth increase and decrease upon testing conditions, as well as the mechanism of depth decrease, still remain uncertain. This chapter investigates the relative contributions of contact area conservation, elastic recovery, and pile-up development to the depth evolution in this transition region. Single asperity wear experiments were conducted in polycrystalline austenitic steel, copper, and cementite to provide a comparative analysis for multiple materials during the initial wear stage. Two sphero-conical nanoindenter tips were used to examine the effect of the size of contact area as well as the contact angle. In addition, grain orientation dependent experiments were carried out to discuss the orientation influence on plastic plowing.

6.2 Results

6.2.1 Overview of transition from indentation to plastic plowing

We demonstrate the typical wear track shape for cementite (Fe₃C) and austenitic steel (γ -Fe) using the 100 mN wear tracks produced by the 5 µm tip (Fig. 6.1). The pre-scan, wear track and post-scan were used to determine the elastic and plastic depth. The fractions of elastic and plastic depth in the steady state region are 83.8% and 16.2% for cementite and 53.5% and 46.5% for austenitic steel, respectively. Specific values of the penetration depth

⁸ This chapter is based on: H. Tsybenko, W. Xia, G. Dehm, S. Brinckmann, "On the commensuration of plastic plowing at the microscale", Tribology International 151, p. 106477, 2020

 $(h_{init}, h_{ind}, h_{avg})$ and distance (d_{init}) are shown for the austenitic steel wear track (Fig. 6.1b), and these values are determined for all forces and materials.



Fig. 6.1. Depth curves for the 100mN wear tracks made by the 5 μ m tip in (a) cementite (Fe₃C) and (b) austenitic steel (γ -Fe).

Generally, the wear track segment (red curves in Fig. 6.1) begins with the smoothly increasing penetration depth in cementite and austenitic steel after indentation. In cementite, the initial depth maximum h_{ind} during the initial wear segment is comparable to the indentation depth h_{ind} (see inset in Fig.6.2a), whereas the difference between indentation depth and initial depth maximum is more prominent in austenitic steel. For copper, the behavior is similar to austenitic steel and is not shown here for conciseness (Fig. B1 in Appendix B). The depth has its maximum at a distance d_{init} of ~18 µm and ~10 µm for cementite and austenitic steel, respectively. Afterwards, the depth reaches a steady state in cementite (Fig. 6.1a) and does not change significantly thereafter. By contrast, in austenitic steel (Fig. 6.1b), we notice a gradual decrease in the penetration depth, i.e. the depth maximum. This decrease effect was observed for all wear experiments for austenitic steel and copper. In cementite samples, the depth never experienced the decrease.

In the steady-state region of the wear experiment, the depth remains rather constant in cementite. In contrast, the post-scan profile reveals much larger depth fluctuations in the ductile metals. The wear mechanisms during this stage are not part of the present analysis and not elaborated further.

6.2.2 Analysis of transition mechanisms

We determine whether the initial depth increase is a measurement artifact of the nanoindenter dynamics. To this end, we performed wear experiments with increasing length (2 to 20 μ m) in [001] and [111] austenitic steel grains (identified via EBSD) using 5 μ m sphero-conical diamond tip. In each grain, one set of wear tests was conducted each for the test protocol with and without a 5s holding period after the wear segment and before the unloading segment.



Fig. 6.2. Secondary electron images of wear tracks without holding between wear and unloading segment with 40 mN normal force in a [001] austenitic steel (γ -Fe) grain: (a) 2 μ m, (b) 6 μ m and (c) 10 μ m wear length. The white arrow in (c) shows the wear direction for all tracks, white asterisks and triangles mark the pile-up and the approximate position of the initial contact, respectively.

As shown by SEM in Fig. 6.2 for the [001] grain, plastic plowing in austenitic steel is accompanied by the formation of extensive plastic zones and pile-up at the sides and in front of the wear track as well as activation of multiple slip systems in the grain. The plastic zones and pile-up grow considerably with increasing wear length.

After performing wear experiments, confocal measurements of the wear tracks were carried out. The penetration depth curves with a 5 s holding time coincide (Fig. 6.3a) and the maximum depth is reached at a wear track distance of ~6.5 μ m. It is observed that no change in the depth occurs due to the holding period. When comparing average curves for the [001] and [111] grains (Fig. 6.3b) with and without holding time, one notices that the initial slope of the depth curve, the maximum depth, and length of a transition region (~8 μ m, marked by the black arrow) are independent of the crystallographic orientation and the holding time. However, the decreased wear depth for long wear tracks, i.e. the steady-state depth, depends on the grain orientation. The experimental curves show similar behaviors with and without holding time even for long wear tracks.



Fig. 6.3. Profiles along the wear tracks in single grain of austenitic steel (γ -Fe) using confocal measurements. (a) Depth curves for wear tracks with a normal force of 40 mN in a [001] with a 5 s holding time after the wear segment, (b) Depth curves for 20 µm long wear tracks in [001] and [111] grains with and without holding segment after the wear segment. The black arrow marks the end of the transition region.

6.2.3 Analysis of both stages of the transition region

We now consider the influence of the normal force on the initial depth increase for different materials. Fig. 6.4a shows the ratio of the initial depth maximum and the indentation depth. For cementite, the initial depth maximum is ill-defined due to the unclear depth decrease. For cementite, the maximum depth in the first 20 μ m is used as the initial depth maximum. Additional data points were added from [135] to compare the depth between a spheroconical tip (this investigation) with a Berkovich tip in edge forward (EF) and face forward (FF) orientations. Expected depth increase values according to geometrical scaling laws for three orientations (section 6.3.1) were added to the vertical axis.

After indentation, the penetration depth increases for all materials and for the entire normal force range, i.e. all ratios are larger than 1.0. At lower normal forces, the depth ratio is ~1.2 and the ratio remains constant up to 20 mN. Above 20 mN, the ratios for copper increase. In this force regime, differences between the two tip radii occur: the ratio increases drastically with the 5 μ m tip. The data points for the sphero-conical indenter in copper are located between data for the edge forward and face forward orientations for a Berkovich tip [135]. Although initially closer to edge forward data points, the ratio for the 5 μ m tip is becoming more similar to the face forward data with increasing normal forces. For austenitic steel, the ratio remains constant even for with higher forces. For cementite, the depth ratio remains constant and is lower than for the ductile materials. There is also no effect of the tip radius for cementite.



Fig. 6.4 (a) Initial depth maximum normalized by indentation depth as a function of the normal force. Data points for copper (Cu) and a Berkovich tip in two orientations were added [135]. FF, EF, and S denote expected ratio values for face forward and edge forward Berkovich tip orientations and spherical tip respectively. (b) Initial depth maximum normalized by average depth as a function of the normal force. Data points for each wear test are marked with circles, while lines denote the average values (vertical strokes). The circle size denotes the radius of the indenter tip.

As the next step, we inspect the penetration depth decrease to the steady-state region of the wear track (Fig. 6.4b). The initial depth maximum was normalized by the average depth in the steady-state region. The depth ratio in Fig. 6.4b scatters significantly for lower forces due to the bigger influence of initial surface roughness. For higher normal forces, the ratio remains constant, i.e. it is independent of the normal force. For cementite, the depth decrease is absent and the ratio remains stable at 1.0. However, the initial depth is ~1.5 times the steady-state depth for all normal forces in the more ductile copper and austenitic steel. It is observed that in copper experiments with a 20 μ m tip, the ratio of initial depth maximum and average depth is much higher than for the 5 μ m tip.

Finally, the position of the initial depth maximum (d_{init}) along the wear track was examined. It should be noted that the maximum depth position is partly influenced by the lateral compliance of the experimental setup as discussed subsequently. Fig. 6.5 demonstrates the distance of the depth maximum to the indentation point as a function of the normal force. Please note that we omitted cementite because of the undefined position of the initial maximum. One observes a linear dependence of the initial depth maximum is significantly elevated for the smaller indenter tip in copper. However, the position does not scale with the indenter radius. The increasing distance of the depth maximum and hence the increasing distance until reaching the steady-state depth suggests that the transitional region grows as well with increasing normal forces. As in the single grain experiments in

austenitic steel (Fig. 6.3a), where the distance to the maximum penetration depth is larger than the 5 μ m tip radius, in long wear track experiments in copper and austenitic steel after reaching a specific normal force, the maximum penetration depth distance exceeds the value of the tip radius. This implies the presence of another mechanism that causes gradual penetration depth evolution in the transition region as opposed to the ideal plastic behavior which would cause an immediate sinking of the indenter tip at a comparable distance to the tip radius (section 6.3.1). An alternative explanation based on the lateral compliance is discussed in the next section.



Fig. 6.5. Distance between the indentation location and the location of the initial depth maximum d_{init} as a function of the normal force. Dashed lines represent fitted linear functions with the given slope. The circle size denotes the radius of the indenter tip.

6.3 Discussion

This analysis aims to describe qualitatively the initial stage of plastic plowing. We observe that the penetration depth curves are overlapping irrespective of lengths in austenitic steel grains (Fig. 6.3a). Furthermore, the depth curves overlap in the transition region for the [001] and [111] grains (Fig. 6.3b) but show a significant difference in the steady-state region due to the crystal orientation, i.e. plastic anisotropy. Including a holding segment after the wear segment leads to no change in the penetration depth (Fig. 6.3a). These observations prove that the initial depth increase is not due to the nanoindenter dynamics and control loops but a material dependent mechanism.

Based on the results, we discuss the initial two stages of wear, i.e. the transition from indentation into the steady-state regime (Fig. 6.6). In the first stage, the depth increases

after the beginning of the lateral movement and the total force vector reorients from the normal into a tilted direction. This reorientation leads to the change from the symmetric initial contact to the one-sided contact during wear, which is the widely accepted cause for the initial depth increase [122,135,137]. In this analysis, we also observed the second stage after reaching the maximum depth [137]. In this stage, the pile-up provides an additional contact area and thus leads to a decrease in depth. This depth decrease is accompanied by an increase of pile-up in the front and on the side. The transitional segment is followed by a steady-state region in which the individual grain orientation dominates the wear track depth.



Fig. 6.6. Schematic of a transition from indentation to plastic plowing during microscale wear. Blue, red and green lines represent the contact area during indentation, transition, and steady-state stages, respectively. A dashed red line illustrates the remaining elastic contact at the beginning of the transition region. The red arrows mark the direction of the elastic recovery during the transition.

6.3.1 First stage of transition from indentation to plastic plowing

Initially, we discuss the first stage of the transition for metals like austenitic steel and copper. When using a Berkovich tip in the face forward or edge forward orientation for the wear experiment [135], the depth is expected to increase by a factor of $\sqrt{3}$ or $\sqrt{3/2}$, respectively, to conserve the contact area after the indenter begins to move laterally (FF and EF on Fig. 6.4a). The present study uses sphero-conical indenters, implying that the penetration depth is expected to grow by the factor $\sqrt{2}$ (S on Fig. 6.4a). When inspecting the ratios between initial depth maximum and indentation depth for copper (Fig. 6.4a), the ratio is consistently $\sqrt{2}$ for normal forces ≤ 20 mN, i.e. the same force range as in [135]. Hence, the depth evolution follows from the conservation of the projected contact area in the surface normal direction. As the hardness of the material and the normal force remain constant, the projected contact area remains rather constant although shape changes occur. However, the conservation of the contact area does not clarify the drastic increase

of the ratio for the 5 μ m tip in copper for normal forces \geq 50 mN. Moreover, this explanation does not address the smooth transition (marked by the red A - B in Fig. 6.6) from indentation to the initial depth maximum. The smooth transition is not due to a dynamic effect or due to the nanoindenter dynamics, as discussed before.

We discuss the gradual depth increase up to its maximum value. If this initial depth increase was solely related to the reduced contact area, one would expect an immediate sinking of the tip to the maximum depth as soon as the tip starts moving laterally. Even though work hardening occurs during plastic plowing, those dislocation mechanisms are much faster than the stage movement and thus do not affect the penetration depth. The linear dependence of the position of maximum depth on the normal force (Fig. 6.5) indicates that the indenter tip moves along the same slope irrespective of the normal force. A similar agreement of initial slopes was also observed for fused quartz [122] but not discussed nor reasoned. Furthermore, a tip size effect exists: the 5 μ m tip requires a 2.2 times longer path to reach the maximum penetration than the 20 μ m tip for the same normal force (Fig. 6.5).

The lateral instrument compliance is a possible cause for the gradual depth increase instead of the rapid sinking. Due to the lateral compliance, a slight tilt of the tip assembly may lead to the smooth depth slope at the beginning of the lateral movement. On the contrary, numerical studies of wear [136–138] exclude any lateral compliance – however – the depth increase is similar to the ones obtained in this study. Moreover, the transition to the depth maximum depends significantly on the tip radius (Fig. 6.5) which is uncorrelated to the lateral compliance. Therefore, lateral compliance cannot be the cause of the smooth transition from indentation to the maximum depth.

We profiled the 20 μ m long wear tracks without a holding segment (Fig. 6.7). These profiles were obtained along and across the wear direction at the point of the maximum depth (marked by a red cross in Fig. 6.7a).


Fig. 6.7: (a) Location of the profiles for the 20 μ m long wear tracks in austenitic steel (γ -Fe). The red cross marks the lowest point in the transition region. (b) Profiles along and across wear direction in [111] and [001] grains.

As shown in Fig. 6.7b, the profiles along and across the wear track coincide initially, i.e. the wear groove and the initial slope have the same shape as the indenter tip. However, the slope changes rapidly as the tip approaches the deepest position. As in the previous measurement including holding times (Fig. 6.3), there is no grain orientation dependence on the groove shape as well as on the initial depth increase. This observation implies that the elastic anisotropy plays an insignificant role in the first stage of the transition region.

The elastic recovery was previously studied for metals during indentation [224] and the viscoelastic recovery was determined for polymers [139–141]. However, we argue that the gradual initial depth increase is attributed to the elastic recovery behind the indenter tip, i.e. on the backside of the indenter tip (see Fig. 6.6). At the beginning of the transition from indentation to plowing, the backside of the tip loses slowly contact with the metal. This reduction of contact causes the initiation of elastic recovery on the backside of the indentation (marked by red arrows in Fig. 6.6). Simultaneously, the depth increases due to reduced elastic contact. Therefore, the contact area reduction does not happen immediately and the depth increases gradually. This gradual transition could be envisioned falsely as an indenter tip sliding on the material groove that was produced during the initial indentation. This mechanism does not occur because there is a shift in the profile and a change of the slope along the wear track (Fig. 6.7b). Both observations are inconsistent with the sliding-down mechanism. Hence, the smooth elastic recovery on the backside is the only mechanism that explains the experimental observation. The effect of elastic anisotropy is rather not strong since the curves for the profiles along the wear direction for [001] and [111] grains coincide.

The transition from indentation to the maximum depth is much longer for the softer copper than for the harder austenitic steel (Fig. 6.5). The enhanced compliance of copper, i.e. smaller Young's modulus, results in a longer elastic interaction distance and hence longer transition. The tip with the smaller radius (5 μ m tip in copper) penetrates the material deeper than the tip with the larger radius (20 μ m tip in copper). The elevated penetration and the smaller tip curvature result in the larger contact angle with the material on the backside. As a consequence, the direction of elastic material recovery is more towards the wear direction as the 5 μ m tip moves forward (as it is in case "A" on Fig. 6.6). By contrast, the direction of elastic recovery is almost normal to the initial surface as the 20 μ m tip moves, due to the smaller contact angle (as in "B" on Fig. 6.6). Therefore, the elastic interaction distance is longer for the 5 μ m tip. The comparisons of different materials and tip radii support the elastic recovery resulting in the smooth transition from indentation to the maximum depth. Furthermore, the projected contact area is conserved.

The friction coefficient is interrelated with the elastic recovery and pile-up development and is an important factor for the evolution of the wear depth. The development of the friction coefficient during the transition from indentation to wear has the same tendency in ductile metals (this study) as for fused quartz [122]. However, the lateral force measurements of the nanoindenter are inaccurate, especially for small forces. Due to the unreliable lateral forces, we omit the discussion of the interaction of the friction coefficient and plastic plowing during the transition from indentation to wear.

6.3.2 Second stage of transition from indentation to plastic plowing

Now we discuss the second stage of the transition for metals, i.e. from the initial depth maximum to the steady state regime in which the pile-up and depth evolution are hypothetically related. We analyze the confocal data for the front pile-up volume for wear tracks without a holding segment in austenitic steel. The pile-up volume in front of the indenter tip is defined by the base height and the cross-section at the end of the experiment (Fig. 6.8a). The light-blue and pink regions show the base height and the pile-up domain, respectively (see Fig. 6.8a inset).

Fig. 6.8a demonstrates a steep growth of the front pile-up volume with increasing wear track length. A steady state volume of the pile-up is reached at ~8 μ m, which is equivalent to the transition length in the depth curves (Fig. 6.3b). The pile-up volume is greater by 11.5% in the [001] grain than in the [111] grain in the stable regime. Hence, the crystal structure influences the pile-up volume in front of the indenter tip. This observation

highlights that the [111] grain has an easy glide normal direction and results in a small front pile-up.



Fig. 6.8. (a) Pile-up volume in front of the indenter tip as a function of the wear track length. The inset shows the pile-up domain that is determined from the zero height. The black line illustrates a typical cross-section for the estimation of the side pile-up and groove areas, (b) Side pile-up areas and groove areas as a function of the distance along the wear track. The bottom filled triangle represents the groove, which is below the reference height and the top filled triangle represents the pile-up which is above the reference height. The inset shows the wear groove and pile-up area in the [111] grain.

It is worth discussing the measurements of the pile-up volume and contact area. The pileup volumes and areas depend on the base height, which has a small scatter and hence the shape of the observed curves remains unaffected. Furthermore, chip formation and expulsion would deflate the front pile-up volume at higher normal forces or larger attack angles [32]. However, this chip formation was not observed here (Fig. 6.2). Moreover, the post-deformation measurements do not address the elastic contact and surface-tip adhesion during the experiment. The material transfer to the diamond tip is not observed during nanoindentation [100], showing that the pile-up and groove area are not influenced by adhesive wear.

The wear track depth and the side pile-up are correlated during the transition from indentation to plastic plowing. For the [001] and [111] grains in the initial transition stage, the curves overlap for the groove cross-section area, which are represented by solid lines in Fig. 6.8b. Here, the groove cross-section area is defined as the area between the base height and the wear track depth for the 20 μ m wear tracks. This overlap of the curves for the groove cross-section area supports the hypothesis that elastic recovery – and not the grain orientation – determines the transition until the initial depth maximum. Since the side

pile-up areas remain constant until the initial depth maximum is reached, this side pile-up appears during indentation. After reaching the maximum, the depth decreases and the side pile-up areas show different trends in the [001] and [111] grains. While the side pile-up area decreases briefly or remains constant in the [001] grain, the side pile-up area gradually increases in the [111] grain. Finally, also the side pile-up grows rapidly for the [001] grain. The maximum error was calculated as ~10% at the position of the initial depth maximum and decreased to less than 1.5% in the final transition and steady-state regions because the side pile-up have a larger area in the latter regions. Fig. 6.8b includes additionally the steady-state groove and pile-up areas, which were determined by averaging profiles with a 0.1 μ m separation in the steady-state region from 12-18 μ m. These steady-state side pile-up and wear groove areas are larger in the [111] grain than in the [001] grain. Hence, the removed material in the wear track is correlated to the side pile-up in the transition zone and in the steady state zone. Please, note that the wear direction with respect to the crystal orientation influences the pile-up area and groove area. These considerations should be addressed in future studies.

We analyze the side and the front pile-ups to investigate further the transition region. At the beginning of the lateral movement, the volume of the front pile-up is rapidly increasing while the side pile-up area remains constant. As the penetration depth reaches its maximum, the front contact area increases and supports the normal and tangential forces. As the indenter tip moves forward, the front pile-up volume increases constantly until it reaches the steady-state volume at the end of the transition region (~8um, see Fig. 6.8a). The front pile-up increase is followed by a decrease in the wear groove size and depth, to conserve the projected contact area. While the front pile-up increases, the side pile-up develops as well. In the second stage of the transition region, the grain orientation determines the pile-up evolution and the penetration depth. As shown in Fig. 6.8b, the side pile-up grows faster in the [111] grain. The front pile-up volume is larger for the [001] grain than the [111] grain, while the depth decrease in [111] grain is slower than for the [001] orientation. Therefore, the influence of the front pile-up on the wear groove formation is significant. Similarly, the dominant resistance to plastic plowing is provided by the material in the wear direction (front contact area).

We discuss the results of cementite in comparison to austenitic steel and copper. The comparison of austenitic steel and copper reveals the influence of Young's modulus on the transition distance from indentation to the initial depth maximum. It is shorter for austenitic steel (E = 210 GPa) because it is stiffer than copper (E = 128 GPa). Even though cementite has similar elastic modulus as austenitic steel, because cementite is

much harder than austenitic steel and copper, less pile-up develops during the wear experiment in cementite and this small pile-up does not significantly increase the contact area during plastic plowing (see Fig. 6.1). Therefore – after reaching the maximum depth, the wear depth remains constant for the remainder of the wear track (Fig. 6.4b). This argument also applies to fused quartz, in which no depth decreases after the initial depth maximum was observed [122]. Therefore, the interaction of pile-up development, wear depth and elastic recovery is evident also from the difference in the transition from indentation to wear in hard and soft materials.

Concluding, several factors determine the wear depth during the transition from indentation to wear. In the first stage of this transition, the conservation of contact area leads to the depth increase and the elastic recovery determines the slope of the depth curve. The elastic recovery provides an additional contact area. However, the magnitude of the elastic recovery on the backside is constantly decreasing during the first stage. As the asperity moves laterally, the front pile-up gradually increases and provides an additional contact area at the front of the tip. This process causes the subsequent depth decrease in the second stage of the transition region. Hence, while the conservation of the contact area is the main factor that determines the wear depth evolution, elastic recovery and pile-up development are the dominating effects in first and second stages of the transition region, respectively. The position of the maximum depth is determined by the interaction of the three mechanisms.

6.4 Conclusions

The following conclusions are derived from observations of the initial stage of plastic plowing in single-stroke wear experiments:

- The transition from indentation to plowing can be divided into two stages: initial depth increase and subsequent depth decrease. The transition stages are partly understood by the conservation of the projected contact area in the surface normal direction: as the normal force is constant, the projected contact area reshapes but remains of equal size.
- The initial penetration depth increases in all materials and the increase is more pronounced for higher normal forces and more compliant materials. Regardless of the normal force, the maximum depth increases by a factor $\sqrt{2}$ after indentation for

the sphero-conical tips in ductile metals. The length of the initial transition segment depends linearly on the normal force.

- Initial depth increase is associated with the elastic recovery on the backside of the tip which is rather independent of the crystal orientation. At the beginning of the lateral movement, the elastic support on the tip backside smoothly reduces which results in a reshaping of the contact area to support the normal and tangential forces. This mechanism results in a smooth increase of the depth until reaching the maximum depth.
- During the second segment of the transition, the depth decrease is observed only for ductile metals, which develop front and side pile-ups. The contact area increases as a result of pile-up formation in front of the indenter tip. This increase in contact area causes a decrease in penetration depth.
- In the second stage of the transition from indentation, the crystallographic orientation of grains and the relative wear direction determine the front and side pile-ups as well as the decrease of the penetration depth and groove area.

7. Scratch hardness at a small scale: experimental methods and correlation to nanoindentation hardness⁹

7.1 Introduction

The scratch hardness evaluation still remains complementary to indentation with the former confined to a niche segment of thin film and coating analysis. In large part, the constraints of the wear experiment are due to the inability to correlate the scratch hardness to the indentation or nanoindentation hardness. In addition, there is a multitude of wear track width evaluation methods and they influence the scratch hardness. Therefore, it is impossible to compare and discuss reported results. Moreover, the physical mechanisms that are implied for the different wear track width parameters are not fully addressed.

The aim of this chapter is twofold. Firstly, we conduct a comparative analysis of four definitions of scratch contact area and hence scratch hardness. These methods are based on the penetration depth during the wear experiment and groove width measurements after the experiment. Secondly, we examine the correlation between the nanoindentation and scratch hardness. By performing nanoindentation and wear experiments on aluminum (AI), copper (Cu), soda-lime glass (SLG), cementite (Fe₃C), and silicon (Si), we systematically analyze the influence of distinct material properties (for instance, yield stress, Young's modulus) and deformation behavior (sink-in, pile-up) on the scratch hardness and the ratio between scratch and nanoindentation hardness. Although the scratch hardness depth dependence, the influence of the tip size, and contact shape are not the focus of this analysis, we discuss these phenomena and their influence on the scratch hardness. In addition, we address the applicability of the elastic Hertzian solution as a first-order approximation for the contact area during wear.

⁹ This chapter is based on: H. Tsybenko, F. Farzam, G. Dehm, S. Brinckmann, "Scratch hardness at a small scale: experimental methods and correlation to nanoindentation hardness", Tribology International 163, p. 107168,2021.

7.2 Results

7.2.1 Overview of material behavior

As the first step, we inspect the material's response to the tribological load. Fig. 7.1 compares typical imprints in aluminum and cementite obtained by nanoindentation and wear with a 100 mN normal force.



Fig. 7.1. Secondary electron images of the 100 mN imprints in aluminum (AI) and cementite (Fe₃C). Note the scale difference when comparing the individual images. Nanoindentation experiments in (a) aluminum and (b) cementite were performed with a Berkovich tip. Wear tests in (c) aluminum and (d) cementite were conducted using a 5 μ m tip. The white arrows show the sliding direction. (e) Close-up of the wear track in aluminum demonstrating extensive plastic slip at the wear track edge. (f) Close-up of the wear track in cementite showing slip lines and wear debris at the wear track edge.

One observes a drastic difference in materials deformation as a consequence of their intrinsic material properties. Nanoindentation and wear in aluminum result in extensive pile-up formation (Fig. 7.1c) and large imprints. However, the size of the plastic zones is substantially smaller in cementite than in aluminum because these materials are on the

opposite side of the hardness spectrum. Both materials show activation of slip systems and production of wear debris to different degrees (Fig. 7.1e, f). The ductile aluminum shows extensive parallel slip steps on the lower edge while the slip steps in cementite are sparsely distributed. Wear debris consists of many small pieces in cementite, which has an ultrafine-grained structure. The coarse-grained aluminum has only one large flake forming in the front of the wear track. Experiments in silicon, as well as soda-lime glass, lead to small-scale crack formation at the wear track edge (Fig. C1 in Appendix C). Wearinduced fracture is, however, beyond the scope of this study and will not be further discussed.



Fig. 7.2. Application of the Nix-Gao model for nanoindentations performed using continuous stiffness measurement (CSM) on aluminum (AI), copper (Cu), soda-lime glass (SLG), cementite (Fe₃C), and silicon (Si). The hardness values are normalized by the macroscopic hardness. For aluminum and copper (Cu), we omit the datapoints below a threshold of 650 nm as these points do not follow the linear relationship of the curve. The cementite and silicon were indented to a depth of 1000 nm to protect the nanoindenter.

Elastic moduli, as well as nanoindentation hardness, were determined from nanoindentation tests with the continuous stiffness measurement (CSM). As mentioned in section 3.2.2.1, we apply the Nix-Gao model [162] to determine the macroscopic hardness of the materials. This model implies that the plot of the squared hardness H^2 versus the inverse of the penetration depth is linear and its intercept yields the squared macroscopic hardness H_0^2 . An example of the Nix-Gao plot is shown in Fig.7.2. The indentation depth for aluminum, copper, and soda-lime glass was 2 µm, whereas the depth was 1 µm for cementite and silicon. The datapoints at low penetration depths are omitted for copper and aluminum to ensure the applicability of the Nix-Gao model (see section 3.2.2.1). Aluminum

and copper show a hardness-depth dependence with the average characteristic depth h^* equal to 353 nm and 1706 nm respectively. When inspecting soda-lime glass, cementite and silicon, we observe no depth-dependence of the hardness because the Nix-Gao model does not apply for these materials which do not have an excessive amount of geometrically necessary dislocations. Table 7.1 summarizes material properties measured by nanoindentation.

Table 7.1. Young's moduli and hardness measured by nanoindentation and the corresponding standard deviations (SD).

Material	AI	Cu	Soda-lime glass	Fe₃C	Si
H _I (GPa)	0.25	0.44	5.9	11.1	11.9
SD H _I (GPa)	0.01	0.034	0.06	0.54	0.2
E (GPa)	63.7	98.7	74.1	206.5	175.7
SD E (GPa)	0.7	2.7	0.3	3.8	0.7

7.2.2 Comparison of different definitions of scratch hardness

We now inspect the differences of the reported scratch hardness when using different methods to determine the contact area (section 3.2.2.2). The contact area A_S is either defined by:

- 1) $A_S = f(h_c)$ with the contact depth h_c measured by the indenter during the experiment;
- 2) $A_S = f(w_{pile-up})$ with the width $w_{pile-up}$ measured as the distance between the highest points of the pile-up in the height profile, which is perpendicular to the wear track;
- 3) $A_S = f(w_{max.slope})$ with the width $w_{max.slope}$ measured as the distance between the points of maximum slope in the height profile, which is perpendicular to the wear track;

4) $A_S = f(w_{surface})$ with the width $w_{surface}$ measured as the distance between the points inside the pile-up and at the undeformed surface height. For this measure, the height profiles perpendicular to the wear track were employed.

The contact depth was determined as the average penetration depth in the steady-state region of three wear tracks. As a result, the average contact depth for each normal force is calculated from more than 9000 datapoints. For the three width measures, the data in the steady-state region was evaluated at 20 perpendicular profiles for 3 wear tracks with identical loading parameters. The average contact areas based on groove width were determined from those 60 datapoints. Since plastic deformation of cementite was not sufficient for post-deformation inspection in all loading cases, only the 20, 50, 100 mN wear tracks with the 5 μ m tip were analyzed with a confocal microscope to measure wear groove width. From the contact area, the scratch hardness H_S is evaluated as given by the previous enumeration.

Fig. 7.3 shows the resulting scratch hardness H_S for copper, aluminum, and cementite as functions of the normal force F_N . Silicon and soda-lime glass demonstrate a similar behavior to cementite (see Fig. C2 in Appendix C) and are not shown here for conciseness. Table C1 and Table C2 in Appendix C contain the average scratch hardness. An overview of the typical relative standard deviations of the scratch hardness values $H_S(h_c)$ and $H_S(w_{pile-up})$ for cementite and aluminum at 10 mN and 100 mN is provided in Table C3 and Table C4. The relative standard deviation for the scratch hardness does not exceed 10% and is in general smaller for $H_S(h_c)$ than for $H_S(w_{pile-up})$. The percent differences between $H_S(h_c)$ and $H_S(w_{pile-up})$ as well as between the scratch hardness measured at 10 and 100 mN are significantly larger. Therefore, the differences due to different measurement techniques and different forces are larger than the measurement uncertainty.

Based on the comparison, we identify a number of material scientific tendencies. First, using the contact depth h_c and the width at the surface level $w_{surface}$ lead to the highest H_s , and these values are similar except for the fluctuations at $F_N < 100$ mN in copper. Second, defining the contact area by the width between the highest pile-up points yields to the largest contact area and smallest scratch hardness $H_s(w_{pile-up})$. Third, $H_s(w_{max.slope})$ values are between the $H_s(w_{pile-up})$ and $H_s(w_{surface})$ values.

Generally, the scratch hardness of cementite (also soda-lime glass and silicon) follows a different trend than that of aluminum and copper. With increasing normal force, H_S is

constantly increasing and approaches an approximately constant value in cementite. In contrast to that in aluminum and copper, H_S either decrease to the approximately constant value (after fluctuations at lower F_N) or decrease continuously ($H_S(w_{pile-up})$ in copper).

Finally, a comparison of the scratch hardness values measured at the highest normal force F_N (100 mN for the 5 µm tip and 200 mN for the 20 µm tip) using tips of two different radii reveals a consistent tip size effect. H_S obtained from wear tracks with the 5 µm tip is higher than H_S determined from 20 µm wear tracks in the majority of cases. The extent of this tip size effect depends on the material and will be discussed below.



Fig. 7.3. Comparison of scratch hardness values calculated using contact depth and three definitions for the wear track width for wear experiments in copper (Cu), aluminum (Al), and cementite (Fe₃C) conducted using (a) 5 μ m tip and (b) 20 μ m tip. The data of silicon and soda-lime glass is in Appendix C. Each datapoint is the average of at least 60 measurements.

As the next step, we examine each of the scratch hardness methods in detail. The scratch hardness defined by the contact depth $H_S(h_c)$ demonstrates the most consistent trend with increasing normal force among all methods. For metals aluminum and copper, $H_S(h_c)$ decreases to the constant value after reaching a certain normal force. For harder cementite (as well as soda-lime glass and silicon, see Appendix C), $H_S(h_c)$ is continuously increasing with higher F_N but never reaches the constant value in the normal force range. The macroscopic $H_S(h_c)$ is evaluated from the 5 µm tip experiments and is found to be significantly higher than the macroscopic $H_S(h_c)$ determined with the 20 µm tip. The differences between the two $H_S(h_c)$ values at the highest force F_N are 23% for aluminum and 33% for copper, respectively. In cementite, the difference is 67%. The reader is reminded that the measurements have not reached their constant values in the load range and that the difference is subject to change if the normal force increases.

In contrast to the $H_S(h_c)$, the scratch hardness values based on the contact width measurements do not demonstrate unified tendencies when plotted versus the normal force for ductile metals. Both $H_S(w_{surface})$ and $H_S(w_{max.slope})$ increase at smaller normal forces in 5 µm tip experiments in aluminum and copper as well as in 20 µm tip experiments in aluminum. This behavior is analogous to the $H_S(h_c)$. However, the wear tracks performed with the 20 µm tip in copper yield a continuously increasing $H_S(w_{surface})$ and $H_S(w_{max.slope})$ with increasing F_N .

The scratch hardness calculated from the width between the pile-up peaks $H_S(w_{pile-up})$ continues to decrease at $F_N \ge 50$ mN for the small indenter tip, whereas other scratch hardness values reach relatively stable values at higher normal forces. Overall, the scratch hardness definitions that use groove width as the basis for the contact area calculation exhibit much larger fluctuations for ductile aluminum and copper than the depth-based method.

Since $H_S(w_{surface})$, $H_S(w_{max.slope})$ and $H_S(w_{pile-up})$ do not always stabilize at higher normal forces, the investigation of the tip size effect at the highest normal forces is qualitative. In aluminum, $H_S(w_{surface})$ is 35% lower for the 5 µm tip compared to the values obtained for the 20 µm tip experiments. The opposite behavior is observed for the $H_S(w_{max.slope})$ and $H_S(w_{pile-up})$ definitions, where the scratch hardness is higher when determined from the experiments with the 5 µm tip. In the case of copper, $H_S(w_{surface})$ and $H_S(w_{max.slope})$ are higher for the smaller 5 µm tip than the larger tip by 26% and 21%, respectively. The difference decreases to 6% when $H_S(w_{pile-up})$ is evaluated. Concluding, a scratch size effect (smaller tips result in an elevated hardness value) is observed in aluminum and copper in most evaluation methods.

Based on the penetration depth measurements, we conclude that only the spherical part of the tip was in contact with the material in most cases. The transition depth was exceeded for copper at $F_N \ge 50 \ mN$ for the 5 µm tip. For aluminum, the transition depth was exceeded at $F_N \ge 20 \ mN$ for the 5 µm tip as well as $F_N = 200 \ mN$ for the 20 µm tip.

7.2.3 Relationship between scratch and nanoindentation hardness

We now discuss the correlation between nanoindentation and scratch hardness. The ratio of scratch and nanoindentation hardness H_S/H_I is the inverse of the ratio between the scratch and indentation contact areas A_S/A_I . Hence, we analyze scratch contact areas A_S according to different methods normalized by the indentation contact areas A_I at specific F_N . For each normal force, the indentation contact area A_I was determined from the nanoindentation hardness equation (3.2), while using the macroscopic hardness as evaluated by the Nix-Gao plot (Fig. 7.2).

Fig. 7.4 illustrates the contact area ratios as a function of the normal force. The thin solid black line $A_S/A_I = 1$ represents the equality of nanoindentation and scratch hardness. All other lines and data points are colored with respect to the material's position on the qualitative hardness scale. The dotted lines represent the A_S/A_I with scratch contact area calculated from analytical Hertzian solution $A_{S,Hertz}$, eq. (3.9). Solid and dashed lines correspond to the contact area ratios with $A_S(h_c)$ determined from contact depth and $A_S(w_{pile-})$ with the width between pile-up peaks, respectively. In this figure, we use $A_S(h_c)$ and $A_S(w_{pile-up})$ because they provide the upper and lower boundaries for the scratch hardness and the other area measures are in between those bounds. The normalized $A_S(w_{max.slope})$ as well as $A_S(w_{surface})$ are demonstrated in Fig. C3. Table C5 and Table C6 contain all contact area ratios.



Fig. 7.4. The ratio of scratch to indentation contact areas for wear experiments conducted using (a) 5 µm tip and (b) 20 µm tip. The line color is given by the qualitative hardness scale and represents the material: aluminum (AI), copper (Cu), soda-lime glass (SLG), cementite (Fe₃C), and silicon (Si). The line style represents the scratch contact area method: the dotted line depicts the area $A_{S,Hertz}$ according to the Hertz solution, the dashed line denotes the area $A_S(w_{pile-})$ according to the width at the pile-up peak and the solid line represents the area $A_S(h_c)$ using the contact depth. These values are normalized by the contact area according to the nanoindentation hardness. A horizontal line $A_S/A_I = 1$ depicts the case of equivalent scratch and nanoindentation hardness. Each datapoint is the average of at least 60 measurements.

Generally, the contact area ratio does not reach equality $A_S/A_I = 1$ for any material or tip size in the normal force range. Nonetheless, $A_{S,Hertz}/A_I$ and $A_S(h_c)/A_I$ tend to stabilize to a constant value with increasing F_N . One observes a distinct hyperbolic dependence of F_N for $A_{S,Hertz}/A_I$ as well as $A_S(h_c)/A_I$ in soda-lime glass, cementite, and silicon. The hyperbolic trend in experimental scratch contact area is, however, not present for ductile aluminum and copper.

The Hertzian solution acts as a reference since it is often used in tribology to estimate contact areas and pressures. The Hertzian solution generally results in the lowest ratios A_S/A_I at high forces compared to scratch contact areas determined from experiments. In the lower normal force range, the $A_S(h_c)/A_I$ ratios closely resemble the $A_{S,Hertz}/A_I$ curves for soda-lime glass cementite and silicon in most cases. For instance, $A_S(h_c)/A_I$ ratios overlap with the $A_{S,Hertz}/A_I$ curves for the 5 µm tip experiments in soda-lime glass and cementite at $F_N \leq 20$ mN as well as for the 20 µm tip experiments in soda-lime glass and silicon at $F_N = 10$ mN. The discrepancy between $A_{S,Hertz}/A_I$ and $A_S(h_c)/A_I$ for soda-lime glass, cementite and silicon gradually increases with the higher F_N for both tips. For aluminum and copper, the $A_{S,Hertz}/A_I$ ratio approaches zero and strongly deviates from the $A_S(h_c)/A_I$ ratios.

The area ratio that employs the scratch contact area evaluated from the width between the pile-up peaks shows no distinct trend. In the case of cementite and the 5 µm tip, the $A_S(w_{pile-up})/A_I$ (as well as $A_S(w_{max.slope})/A_I$ and $A_S(w_{surface})/A_I$ see Appendix C) somewhat decreases (similar to the Hertzian solution) and reaches the constant value at a normal force of 50 mN. In copper, the $A_S(w_{pile-up})/A_I$ ratio gradually increases with F_N in 5 µm tip experiments, whereas in 20 µm tip experiments it remains rather constant. In aluminum, $A_S(w_{pile-})/A_I$ fluctuates significantly in 5 µm tip experiments and consistently increases above $A_S/A_I = 1$ for the 20 µm tip. Other scratch contact area definitions (see Appendix C) do not demonstrate a clear correlation with the indentation contact area either.

We analyze the tip size effect on $A_S(h_c)/A_I$ for aluminum and copper, since the ratios reach a constant value at higher F_N , i.e. are independent of the normal force. The constant $A_S(h_c)/A_I$ values for 5 µm and 20 µm tip experiments in copper are 0.28 and 0.38, respectively. For aluminum, the ratios are equal to 0.47 for the 5 µm tip and 0.61 for the 20 µm tip. These observations indicate a tip radius effect on the relation between scratch and nanoindentation hardness.

7.3 Discussion

Based on the results, we discuss the four methods for contact area evaluation, the scratch hardness dependence on the wear conditions as well as correlations between scratch and nanoindentation hardness. The scratch hardness according to Williams [39] is defined by the normal force and projected contact area. The friction coefficient directly influences the evolution of the contact area during wear, however, the contribution of friction is outside the scope of this investigation.

7.3.1 Which wear track groove parameters give the most reliable scratch hardness?

We investigate how the scratch contact area is evaluated and how those contact area values influence the scratch hardness. We consider the physical reasoning behind the selection groove parameters for the contact area calculation.

- Representing the groove width as the distance of pile-up peaks ($w_{pile-up}$) implies that a fraction of the side pile-up provides an additional contact area, which is supporting the normal force. Consequently, the traditional method of contact area evaluation $w_{pile-up}$ leads to the lowest scratch hardness values (Fig. 7.3).
- Similarly, it is observed that the distance of the points with the maximum slope $w_{max.slope}$ on either side of the groove valley results in a large contact area and low scratch hardness compared to most other methods. This contact parameter w_{ma} .*slope* can be interpreted as the contact area width between the indenter tip and surface, which also includes a section of the side pile-up.
- In contrast, the valley width at the surface-level $w_{surface}$ suggests that the side pile-up does not contribute to the contact area. Since $w_{surface}$ is measured at the surface level and h_c is related to the initial surface level, the methods to evaluate $A_S(h_c)$ and $A_S(w_{surface})$ yield similar scratch hardness values, as shown in Fig. 7.3.
- The scratch hardness based on the contact depth $H_S(h_c)$ shows the most consistent behavior among all investigated methods.

Finally, we discuss whether the side pile-up yields to the contact area during wear. In the Chapter 6, we demonstrated the correlation between the side pile-up and wear track depth evolution in austenitic steel during the initial stages of wear. It was shown that the development of the front pile-up (in the wear direction) – and not the side pile-up – provides the dominant resistance to plastic plowing and plays a leading role in the groove formation. However, one has to consider the front and side pileup contributions for the load-bearing contact area.

7.3.2 Critical discussion of measurement artifacts

Artifacts in the wear track width evaluation: The scratch hardness values according to the wear track width measurements change strongly for copper and aluminum (Fig. 7.3) and several factors are responsible for inconsistent trends of scratch hardness when employing the groove width as basis for the analysis. In crystalline materials, the pile-up evolution is governed substantially by the crystallographic orientation of the grain as well as the relative orientation between the grain and indenter tip during wear [160,225,226]. In addition, artifacts, i.e. local height fluctuations occur in confocal microscopy. To minimize these effects, we averaged multiple cross-sections and multiple wear tracks (section 3.2.1).

The accuracy of the wear track width evaluation depends also on the wear conditions. If the surface roughness and side pile-up height are of the same size, the groove width measurement is difficult [123]. This obstacle is particularly relevant for hard materials and low normal forces where only a minor side pile-up develops during wear. Another source of error is the detachment of the side pile-up during chip formation. In steels, the increase in normal force during wear leads to the transition of the wear mechanism from plastic plowing to the combination of plowing and microcutting, i.e. detachment of material [227,228]. The sideway plowing and microcutting result in over-hanging material, which is less elastically supported and therefore contributes less to the contact pressure. As a result, the pile-up has to increase to support the entire applied contact force, resulting in an increase in the contact area. This increase in the contact area is evident by the decrease in apparent scratch hardness for large forces in plastic materials. The onset of chip formation is a possible cause for the continuous decrease of $H_S(w_{pile-up})$ with increasing normal force in copper and aluminum.

The contact depth during wear is affected by the individual grain orientation and proximity to parallel grain-boundaries. These factors are reduced because the contact depth was

determined as the average depth in the steady-state region of the wear track and the wear track length significantly exceeds the grain size. During the pre-scan, the initial topography along the wear direction is recorded to account for the influence of the initial surface roughness and tilt.

Nominal vs. real tip dimensions: For the contact area evaluation using the penetration depth during the experiment, the tip shape has to be evaluated. However, the actual shape of the indenter tip generally deviates from its nominal shape. SEM imaging only provides a 2D representation of the 3D body. Confocal imaging is non-applicable because of the low reflectivity of the diamond tip and AFM is not applicable because of the large slopes in height. Even knowing the 3D shape, one needs to know the orientation of the 3D tip during wear. In this investigation, we assume rotational-symmetrical sphero-conical tips. The nominal tip shape was used for the analysis of the scratch contact area as a first-order approximation. The maximum differences from the nominal tip radii analyzed before wear experiments via SEM are 10% and 7% for 5 μ m and 20 μ m tips, respectively. The deviations from the nominal cone angles are 2.8% for 5 μ m tip and 0.3% for 20 μ m tip.

Elastic vs. plastic contributions to contact area: It should be mentioned that the contact depth during the experiment is defined as the difference between the initial surface topography (pre-scan) and the surface topography during wear (wear segment, section 3.2.1). Hence, the contact depth h_c contains both elastic and plastic fractions. However, the imprint width was found to not elastically recover after unloading during indentation [224] and wear [134]. This observation implies that the wear track width contains no elastic contribution. Only the wear track depth contains a significant elastic contribution and recovers during unloading. Therefore, both groove parameters (contact depth measures during the wear segment as well as width parameters) represent the wear track groove geometry under load.

Verification of the half-circular shape assumption: Williams [39] postulated that the contact area has a half-circular shape during wear with a sphere. This assumption is used throughout literature, as shown previously. In this work, we use that assumption to allow comparison with other works. However, also analyze the veracity of the half-circular shape assumption and fit an ellipse at the end of the wear track groove for the 20 μ m tip experiments on aluminum and copper (Fig. 7.5a), because the 5 μ m tip have a higher error bar. The ratios between the two ellipse axis are plotted as a function of the normal force (Fig. 7.5b).

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The ellipse ratios are in general smaller than a/b = 1 (horizontal line on Fig. 7.5b) and show the decreasing trend with increasing normal force, which implies that the contact shape becomes elongated in the direction of motion. The overall average ellipse ratio values are 0.887 and 0.892 for aluminum and copper, respectively. The average ellipse ratio changes in the range of 0.97 to 0.76 for aluminum and in the range of 1.01 to 0.83 for copper. One notices that in the lower normal force range, the scatter of the ellipse ratio a/b is higher. This scatter is due to the fewer pixels available for the ellipse fitting for narrow wear tracks.



Fig. 7.5. (a) Example of the ellipse (dotted line) fitting at the end of the wear track groove for a 100 mN experiment with the 20 μ m tip on aluminum and copper (Cu). The colored scale demonstrates the surface elevation as measured by the confocal microscope. The dashed line represents the intersection of the groove side walls with the surface (zero height) level. (b) The ratio of the two ellipse axes as a function of normal force for the 20 μ m tip wear experiments on aluminum and copper. A horizontal line a/b = 1 denotes a circle.

Concluding, the a/b ratios are close to 1 and the assumption of a half-circular projected scratch contact area at a surface level is a reasonable assumption in the analyzed normal force range. The decreasing trend in a/b demonstrates the increasing deviation from this assumption at higher forces. It is plausible that the elliptical shape arises from the different unloading in the direction of wear and in its transversal direction. In this understanding, the width decreases more than the front-half during unloading. Another explanation for the elliptical shape of the wear groove is that the tip shape is elliptical. In this explanation, the wear of the diamond tip progresses more on the side of the tip than on the front. This explanation is discarded: the tip wear and the elliptical shape of the diamond should be

more present at low depths. These low depths are utilized at low normal forces. However, the elliptical shape is not observed at these forces.

Since the a/b ratio remains close to 1, and the origin of an increasingly elliptical shape with increasing normal force remained obscure, we follow the scientific community by using the half-circular assumption proposed in the Williams model [39] also in this analysis.

7.3.3 Scratch size effects

We identify the correlation of $H_S(h_c)$ with respect to the wear track depth and indenter tip radius. We observe a distinct difference in scratch hardness as a function of the normal force for materials with different nanoindentation hardness.

The scratch hardness of metals copper and aluminum has similarities to the indentation size effect [162,165], decreasing hardness to an approximate constant value at higher normal forces and depths. For crystalline metals, the indentation size effect is governed by the geometrically necessary dislocations in close vicinity to the surface [165]. Other proposed mechanisms that control indentation size effect in ceramics and rutile oxides are phase transformations, crack formation, and the mixed elastic-plastic deformation response at higher forces which result in a more compliant material with a larger contact area and lower hardness value [229–231]. A relation between scratch hardness and contact depth was reported by Kareer et. al [35] for the experiments with a Berkovich tip on single-crystal copper. In that article, it was shown that the scratch hardness decreases with increasing contact depth in face-forward and edge-forward orientations. This study shows the same behavior for aluminum and copper during wear with a spherical tip.

In contrast, $H_S(h_c)$ of cementite (as well as soda-lime glass and silicon, see Appendix C) increases with increasing normal force and gradually approaches the constant value. This is the first time, the reverse scratch hardness-depth dependence is shown. As mentioned in section 3.2.2.2, the definition of the scratch contact area $A_S(h_c)$ includes elastic contributions. For materials (e.g. cementite) that have small ratios of Young's modulus to hardness [99] and at small forces, the elastic contribution is large compared to the plastic contribution and leads to deviation of hardness, similarly to the deviation in indentation hardness as reported by Oliver and Pharr [99].

For the metals (AI, copper), we investigate if the scratch hardness dependence on the normal force can be described using the Nix-Gao model [232] in the same way as the indentation size effect is described. In Fig 7.6a, the data deviates from the linear relation

at low penetration depth, i.e. at high values of $1/h_c$. At low penetration depth, also the indentation size effect was found as not applicable [38]. However, at higher penetration depth and lower $1/h_c$, the data points somewhat follow the linear trend. Therefore, the macroscopic scratch hardness $H_{S,0}$ can be calculated at $1/h_c = 0$. We evaluate the $H_{S,0}$ as roughly 0.26 GPa for aluminum and 1.1 GPa for copper measured with 20 µm tip. For the 5 µm tip experiments on aluminum and copper, $H_{S,0}$ values are equal to 0.43 and 1.5 GPa, respectively (see Appendix C). However, since we only have 3 data points and since we extrapolate the scratch hardness to infinite contact depth, the macroscopic scratch hardness has significant uncertainty.



Fig. 7.6. a) Application of the Nix-Gao model for wear experiments performed using 20 μ m tip on aluminum (AI) and copper (Cu). The scratch hardness values are normalized by a resulting macroscopic scratch hardness. b) Application of the Nix-Gao-type model for wear experiments performed using 20 μ m tip on soda-lime glass (SLG), cementite (Fe₃C), and silicon (Si). The data of 5 μ m tip is in Appendix C. Each datapoint is the average of at least 9000 measurements.

In addition, we examine the applicably of the of the Nix-Gao-type model to the scratch hardness of soda-lime glass (SLG), cementite, and silicon and find a linear trend at lower $1/h_c$, with a negative slope. A similar reverse indentation size effect, i.e. decreasing nanoindentation hardness with decreasing penetration depth, was observed only in soda-lime glass, but not in cementite and silicon in this study. Other studies have found also a reverse indentation size effect in soda-lime glass, which was attributed to the formation of cracks during nanoindentation with small active volumes and the loss of the applied energy [231,233].

On the other hand, silicon and cementite have a different size effect during nanoindentation and wear. In silicon, a reverse phase transformation influences the

unloading during indentation [234] but not the hardness during loading. Wear is a process of constant loading and unloading and hence the reverse phase-transformation is influencing wear, where it leads to more reverse phase transformation at higher forces and more contact area reduction during partial unloading in the wear track wake. Hence, the material has higher hardness values at higher forces. The reverse indentation size effect in cementite is attributed to plastic densification, as that material has nanopores in its undeformed state.

The indentation hardness dependence on the tip size was previously found in nanoindentation tests with spherical tips in metallic materials [228,235]. Here, we study the effect of the tip size on the scratch hardness. The investigation of two tips of two different radii but same cone angle reveals the existence of the tip size effect: the tip with the smaller tip radius yields higher scratch hardness. The scratch hardness difference between the two tips is higher for harder materials than for the two metals copper and aluminum (Fig. 7.3). In the article of Cavaliere and Prete [143], the tip size effect on scratch hardness was demonstrated for electrodeposited nickel of different grain sizes. The scratch hardness was higher when using the 0.5 μ m radius than when using 2.5 μ m spherical tips. However, the difference between scratch hardness values of the two tips decreases with decreasing grain size. The tip size effect and its origin were, however, not addressed in that work. We give two explanations for the tip size effect in wear experiment.

- One reason for the tip size effect in wear experiment is the difference in the contact angle between tip and material. A larger contact angle for the smaller tip leads to material being pushed upwards during wear. For the larger tip, the material flows forward and to the side of the indenter, which increases the contact area. Please note that this explanation is not applicable for aluminum at the highest normal force for each tip. In these loading conditions, the conical parts of both tips were in contact with the material resulting in the same contact angle between the tips and the material
- Secondly, during wear the conventional micromechanical size effect is present: smaller areas result in larger plastic strain gradients and elevated geometrically necessary dislocations and hardening.

7.3.4 Correlations between scratch and nanoindentation hardness

We now focus on the ratio of scratch and nanoindentation hardness. The ratio between scratch and indentation contact areas $A_S/A_I = H_I/H_S$ represents the ratio between

nanoindentation and scratch hardness. As was noted before, we identified a monotonic relation of the contact area ratios (Fig. 7.4) only if the scratch contact area is defined by the contact depth $A_S(h_c)$. Therefore, we only use the results of that method and the analytical Hertzian solution $A_{S,Hertz}/A_I$ in this section.

One notices that for harder soda-lime glass, cementite, and silicon the contact area ratio exceeds $A_S/A_I = 1$ at lower forces. At higher F_N , the ratio decreases continuously and gradually reaches a constant value below $A_S/A_I = 1$. There are several possible reasons for the difference in contact areas and hardness in these hard materials. Wear experiment induces a much higher equivalent plastic strain than indentation [150] and hence the material yields during wear at lower normal force than would be required to induce plasticity during indentation. As the material yields at lower normal forces during wear, the scratch contact area is larger than the indentation contact area As the normal force increases, the increase in plasticity and in pile-up [225] leads to a contact depth decrease and a decrease in the contact area ratio below 1. To clarify: during In indentation, the influence of the pile-up on the contact area is smaller than during wear because wear movement, adhesion, and friction cause the formation of higher pile-up volume during wear than during indentation. For instance, some of the piled material in front of the indenter is pushed further and accumulates, thereby resisting plowing during wear. On the other hand, less pile-up forms due to the absence of the wear movement during indentation. Therefore, A_S/A_I reaches a value below 1.

As a first-order approximation, we determine the scratch contact area according to the Hertzian solution and normalize it by the contact area due to the nanoindentation hardness definition $A_I = F_N/H_I$ (3). The Hertz equation describes the frictionless normal contact under small strains and elastic deformation. The application of the Hertz equation to the frictional sliding with severe plasticity is a simplification, which is only valid for small normal forces and hard materials, that have a high yield strength. Therefore, the experimental $A_S(h_c)/A_I$ closely resemble $A_{S,Hertz}/A_I$ the for soda-lime glass, cementite, and silicon at the sufficiently small F_N as these materials and loading conditions correspond to the assumptions of the Hertz model.

We use the Hertzian solution to derive a general model for the contact areas. After the transition from indentation to wear, the projected scratch contact area corresponds to the initial indentation contact area because both the hardness of the material and normal force remain the same (i.e. contact area conservation) [225]. Therefore, the half-circular scratch contact area is identical to the Hertzian full circle contact area during indentation in this

first-order approximation. The contact area according to the Hertzian solution normalized by the indentation area follows a hyperbolic trend (Fig. 7.4). This hyperbolic behavior indicates that the contact area ratio is inversely proportional to the normal force. Combining the Hertzian solution (3.9) and indentation contact area according to the nanoindentation hardness definition (3.2), we obtain:

$$\frac{A_S}{A_I} = \frac{\pi \left(3F_N R/4 E_{E_{eff}}\right)^{2/3}}{F_N/H_I} = 1.04\pi H_I E_{E_{eff}}^{-2/3} R^{2/3} F_N^{-1/3} .$$
(7.1)

The $A_{S,Hertz}/A_I$ ratio reaches 0 as the normal force F_N increases. The slope of the hyperbola is defined by the material properties $H_I E_{E_{eff}}^{-2/3}$ and the indenter tip radius $R^{2/3}$. $H_I E_{E_{eff}}^{-2/3}$ is a characteristic material parameter to describe the relative contributions of elastic and plastic strain and it is analogous to the rheological parameter that defines the magnitude of the elastic recovery at specific plastic strain [150]:

$$\varepsilon_e = \sigma_y / E$$
 , (7.2)

where σ_{γ} is yield strength and *E* is the yield strength of the material.

The deviation between the experimental $A_S(h_c)/A_I$ and analytic $A_{S,Hertz}/A_I$ ratios gradually increases with the increasing normal force for soda-lime glass, cementite, and silicon (Fig. 7.4). This growing difference indicates the increase of the scratch contact area due to the plastic deformation and subsequent pile-up formation because the friction results in higher strains. The Hertzian solution is not applicable in these loading conditions.

For ductile aluminum and copper, the ratios $A_S(h_c)/A_I$ remain constant and do not change as F_N decreases. Therefore, the Hertzian solution is not applicable here because the forces are too high to determine experimentally the contact area ratio increase and $A_{S,Hertz}$. Hence, only the constant $A_S/A_I < 1$ segment of the curve is observed for these materials, i.e. scratch hardness remains higher than nanoindentation hardness. Moreover, the extensive plasticity in aluminum and copper explains the absence of hyperbolic behavior in the $A_S(h_c)/A_I$ ratio at even the lowest normal forces.

Summarizing for all materials, we conclude that the ratio between nanoindentation and scratch hardness H_I/H_S approaches a constant value below 1 with increasing normal force. The Hertz elastic solution (11) for the frictionless, small-strain, elastic, normal contact is applied as the first approximation for the contact area during wear of materials

of similar or higher hardness than soda-lime glass in the lower normal force range, i.e., when elastic deformation is dominant. Moreover, the $A_{S,Hertz}/A_I$ provides the lower boundary for the ratio of scratch to indentation contact area at higher forces. However, this discussion does not imply the use of the elastic Hertzian solution to determine scratch hardness, which describes the resistance to plastic plowing.

7.4 Conclusions

The aim of this chapter is to analyze commonly used methods for the evaluation of the scratch contact area and scratch hardness as well as to reveal the relations between scratch and nanoindentation hardness. In addition, we discussed the normal force dependence of scratch hardness and the effect of tip size. The following conclusions are drawn based on the results of this analysis:

- The comparison of four methods to quantify the scratch contact area reveals that the scratch hardness follows a monotonic trend if the contact area is determined from the contact depth during wear. The contact area calculated from the surface level leads to similar values as the method using the contact depth. Using the pileup peaks to determine the contact area results in the largest contact area. Intermediate values are evaluated when the maximum slope is used to calculate the contact area and scratch hardness.
- The groove width measurements are affected by local height fluctuations due to the influence of the crystallographic orientation, surface roughness, measurement artifacts as well as chip formation. These factors are minimized if the contact area is based on the average contact depth in the steady-state region of a sufficiently long wear track.
- In ductile metals copper and aluminum, the scratch hardness according to the contact depth method reveals a conventional force dependence: a size effect similar to that during indentation is present. In contrast, Si, soda-lime glass, as well as cementite, demonstrate an opposite behavior, with scratch hardness gradually increases at the higher normal forces. We propose that these effects are due to densification and reverse phase transformation.
- In addition to the normal force influence, a tip radius effect exists: tip with smaller radii leads to higher scratch hardness. It is proposed that the scratch size effect is

due to the combined influence of the contact angle between the tip and the material as well as the conventional micromechanical (dislocation-based) size effect.

- For all materials, scratch and indentation contact areas are not equal, and the indentation properties are not applicable for wear. The scratch to indentation contact area ratios decrease with increasing normal force (hyperbolic function) for silicon, soda-lime glass, and cementite. For copper, the ratios are equal to 0.28 for 5 µm and 0.38 for 20 µm tip experiments, while for aluminum, the ratios are 0.47 and 0.61 for 5 µm and 20 µm tip, respectively. Hence, the scratch hardness is substantially higher than nanoindentation hardness.
- The elastic Hertzian solution can be applied as a first approximation for scratch contact area estimation in hard materials at lower normal forces and the solution provides a lower boundary for the contact area.

8. Summary

The damage and failure of engineering components due to the abrasive wear often result in immense energy and economic losses. Following this issue, ongoing research focuses on the development of wear-resistant materials for tribological applications, e.g., steels with cementite as a strengthening compound. The wear resistance of these steels largely depends not only on the interaction of cementite precipitates with the matrix but also on the behavior of the cementite phase during contact loading, which has to be better understood. In addition, microscale sliding wear experiments are often employed to investigate the tribological performance, which requires a quantitative measure of wear resistance and clear relations to indentation techniques. In this thesis, a number of tribological and characterization techniques were used to investigate the deformation and chemical behavior of bulk polycrystalline cementite during wear, characterize the relations between indentation and wear and analyze the available models for scratch hardness. This thesis provides findings useful for a better understanding of cementite during the tribological deformation of steels and the development of wear-resistant engineering components with longer lifetimes. Moreover, the work also contributes towards establishing the microscale sliding wear experiment as an indispensable method for approaching the tribological problems on a microscale.

The deformation of the sintered cementite (~95 wt.% Fe₃C) was explored using a singlepass wear experiment performed at the 31 GPa Hertzian pressure and multi-pass sliding wear test at 3.3 GPa. The EBSD slip trace analysis of the single-pass wear track elucidated the activated slip planes, among which the observed (101), (110), and (011) planes are not commonly activated according to the available literature. A following TEM/STEM analysis of both single-pass and multi-pass wear track cross-sections revealed deformed microstructures beneath the contact surface with three characteristic layers, defined through the different distances to the contact surface, shear strains, grain size, and dominant deformation mechanisms. The outermost deformed layer has undergone nanoscale refinement (~10-20 nm grain size) and accommodated plasticity through grain boundary sliding and grain rotation. In the following layer, the fragmented grains had a 100-200 nm size and demonstrated dislocation slip and grain boundary sliding. The deformed bottom layer contains the grains of the initial grain size that are deformed mainly by slip but also by shear bands if the stress intensities are sufficiently high. During sliding wear, cementite ductility is generally enhanced due to the confined volume, shear/compression domination, and potentially frictional heating. However, during the multi-pass experiment, three-body abrasive wear also results in the brittle fatigue crack

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formation on the contact surface. The microstructural alterations and the interplay of strengthening and softening mechanisms during multi-pass wear increase the subsurface nanoindentation hardness by up to 2.7 GPa (17% higher than the initial hardness).

After investigating the deformation mechanisms of cementite below the contact surface, the chemical evolution and phase transformation were also brought into the light by means of TEM electron diffraction, APT, XRD, EDS, AES, and XPS. The Hägg carbide (Fe_5C_2) formation was confirmed in the uppermost deformed regions in the single-pass and multipass wear tracks. The absence of the corresponding Fe₅C₂ reflections on the XRD obtained from the deformed middle layer and the TEM DF images suggested that severe shear strains close to the contact surface were responsible for the transformation to Hägg carbides. Based on the EDS qualitative and quantitative measurements, the intense shearing in the outermost deformed layer also allowed for partial decomposition and mechanical mixing of the remanent non-cementite inclusions into the cementite matrix and the elemental homogenization. Utilizing the results of APT, the potential sources of excess carbon and mechanisms that promote the cementite-Hägg carbide transformation were proposed: tribooxidation of cementite and deformation-induced dissolution of the homogeneously distributed graphite particles. The fractions of phases were quantified from the XPS measurements performed on the wear track array area, and their analysis confirmed the latter hypothesis of graphite decomposition, providing the driving force for the phase transformation. Nonetheless, graphite particles were not fully decomposed and transformed, as was evidenced by AES.

To examine the links between indentation and wear and compare the available models for the scratch hardness, a series of single-pass wear experiments were carried out on several materials with varying mechanical properties and deformation behaviors (aluminum, copper, austenitic steel, cementite, soda-lime-glass, and silicon). The wear track groove geometry was then measured by confocal microscopy. The study of the transition from indentation to wear provided qualitative insights into the factors governing wear track groove formation: the conservation of contact area, elastic recovery, and the front pile-up development. By conducting wear tests with holding segments and different lengths, it was found that the nanoindenter dynamics, i.e., lateral instrument compliance, plays little to no role in the wear track groove development. The experiments on the [111] and [001] austenitic steel grains showed that while crystallographic orientation influence was negligible during the initial increase in wear depth, it has a significant effect during the later stages which are marked by the penetration depth decrease. The investigation continued with the study of the scratch hardness methods and the relationships between the scratch and nanoindentation hardness. The scratch hardness was defined using four scratch contact area methods, and nanoindentation hardness was obtained from the conventional Oliver-Pharr method. According to this analysis, the contact area calculation using the average contact depth as sensed by the nanoindenter in the steady-state wear track region provided the most monotonic trends, consistent values, and a reliable measure for the scratch hardness. In contrast, the groove width measurements were associated with several error sources. A scratch size effect and an inverse scratch size effect were revealed, similar to the indentation size effects, and the Nix-Gao model analogy was applied for the first time to determine the macroscale scratch hardness. The inequality of scratch and nanoindentation hardness was demonstrated by plotting the ratios between scratch and indentation contact areas for a specified normal force range. Nonetheless, the nanoindentation to scratch hardness tends to approach a near-constant ratio below 1 at the higher normal forces, indicating that the macroscale scratch hardness is higher than nanoindentation hardness by a material-dependent factor. In addition, implementing the Hertz elastic solution as a first approximation for scratch contact area provided a good estimation for the hard materials in the elastic deformationdominant force range and a lower boundary for the scratch contact areas overall.

9. Conclusions and Outlook

Based on the investigation in this thesis, some aspects of cementite wear behavior were elucidated, and the obtained results allow for a better understanding of the response of cementite-strengthened steels tribological loading. For instance, the results of slip trace analysis in this thesis together with the present data in the literature, demonstrate that the number of independent slip systems available for the plastic deformation in cementite is sufficient. In addition, shear band formation, nanoscale refinement, and grain rotation in bulk cementite under intense shear strains were observed for the first time. Although the deformation mechanisms in bulk cementite for the two cases of single-pass and multi-pass wear were defined, a question remains about how the activation of these mechanisms depends on the loading conditions, e.g., normal load and strain rate. A systematic investigation based on tribological, and other micromechanical experiments is required to describe the influence of the abovementioned factors. Moreover, since the wear-induced microstructure alterations are related to the changes in the frictional response of materials, the observed cementite microstructure evolution should also be discussed from the point of its influence on friction behavior. This analysis would need additional wear tests with simultaneous recording of tangential force that arises due to friction.

The investigation of the scratch hardness models for the materials of different classes has provided insight into the physical reasoning of selecting a specific model and issues related to various error sources. Since the scratch hardness model based on the average contact depth in the steady-state wear track segment provided the most consistent values, it might be of great interest to implement it as an automated experimental method in the nanoindenter instruments. The scratch size effects were also discussed in this thesis, and for the first time, a model analogous to the Nix-Gao model for the well-examined indentation size effect was applied to the scratch hardness data. It is difficult to assess the model's applicability due to the limited experimental data, and further investigation of the scratch size effects would need experiments conducted in the larger force range. In the case of hard, elastically deforming materials, the scratch contact area is well approximated using the Hertzian static contact model and assuming a half-circular contact area shape. In addition, the elastic model provides a lower boundary for the scratch contact area for the predominantly elastically and plastically deforming materials. Nonetheless, it was shown that the actual scratch contact area tends to deviate from the half-circle and its actual shape has to be further examined for different materials and loading conditions.

Appendix A.



Fig. A1. EDS composition measurements of non-cementite particles in the sintered polycrystalline sample: (a) iron, (b) graphite, and (c) iron oxide. White arrows mark the sequence of data acquisition.



Fig. A2. (a) Wear track cross-section after multi-pass experiment showing a graphite particle in (b). (c) Diffraction pattern showing graphitic reflections.



Fig. A3. STEM BF micrograph of the undeformed cementite sample demonstrating non-cementite inclusions as well as some dislocations (marked by white arrows).



Fig. A4. The region below the wear track and (b) the corresponding EDS spectrum with marked detected peaks.



Fig. A5. SEM image of the 800 x 800 μ m wear track array fragment, demonstrating ~92% coverage of the surface with wear track grooves.



Fig. A6. (a), (b) 3D reconstructions of the APT specimens showing 25 at.% C, 28 at.% C, 30 at.% C. as well as 33 at.% C and 0.3 at.% O isosurfaces. (a) Undeformed cementite grain. (b) Nanocrystalline region below the contact surface. (c), (d) 1D composition profiles for the highlighted cylinders (approx. dimensions 10nmx10nmx80nm) demonstrating iron and carbon content changes in (c) undeformed cementite grain and (d) nanocrystalline region. Dashed lines mark 25 at.% of carbon.

For the undeformed cementite (Fig.A6a), there is a large 25 at.% C isosurface on top of the specimen, attributed to the Ga⁺ contamination during the milling process. At 33 at.% C (Fig. A6a, b), straight columnar structures are related to the crystallographic poles (see section 3.3.4). The stoichiometric composition of cementite is 25 at.%, resulting in the 3:1 Fe/C ratio. Hägg carbide is often noted as Fe_5C_2 , whereas the formula $Fe_{2.2}C$ describes

its chemical composition better [46]. Therefore, the carbon content of Hägg carbide is about 28-31 at.%. Both tips have about 25-33 at.% C, as evident from the tip 3D reconstructions. The measured carbon content is thus higher than expected due to several sources for carbon overestimation in APT (section 3.3.4). The 1D profiles (Fig. A6c, d) show that the average carbon content is 29.63 at.% and 29.23 at.% for the undeformed grain and nanocrystalline region, respectively. This carbon content results in the C/Fe ratios of 0.421 for the undeformed grain and 0.413 for the nanocrystalline region. In addition, in the 1D profiles, the average oxygen contents are 0.03 at.% and 0.05 at.% in the undeformed cementite grain and nanocrystalline region, respectively.



Fig. A7. EDS measurements of the wear track cross-section. (a) STEM bright-field (BF) image of the wear track cross-section after a single-pass experiment with marked characteristic deformed regions [221]: nanocrystalline region (NR) and ultra-fine-grained region (UFGR). The blue dotted line marks the location of the elemental profile line in (b). (b) Elemental profile line showing atomic concentrations of iron, oxygen, and carbon. The dotted line highlights the approximate boundary between the nanocrystalline region (NR) and the ultra-fine-grained region (UFGR).



Fig. A8. SEM images from (a) non-sputtered wear track surface and (b) wear track surface after the 210 min of Ar⁺ sputtering revealing selective etching of iron oxide and graphite particles compared to the cementite. After sputtering the wear track surface, slip traces from UFGR and TR become visible.
Appendix B.



Fig. B1. Depth curves for the 100mN wear track made by the 5 µm tip in copper (Cu).

Appendix C.



Fig. C1. Secondary electron images of the 100 mN (a) nanoindentation and (b) wear imprints in silicon (Si) demonstrating crack formation.



Fig. C2. Comparison of scratch hardness values calculated using contact depth for wear experiments in silicon (Si) and soda-lime glass (SLG) conducted using 5 μ m tip and 20 μ m tip. Data points for two indenter tip radii are represented by circular dots of different sizes. Each datapoint is the average of at least 9000 measurements.



Fig. C3. The ratio of scratch to indentation contact areas for wear experiments in (a) copper (Cu), aluminum (Al), and cementite (Fe₃C) conducted using 5 μ m tip, and in (b) copper (Cu) and aluminum (Al) conducted using 20 μ m tip. The line style represents the analysis method: dotted line depicts the area according to the Hertz solution; the dashed line denotes the area according to the width at the maximum slope and the solid line represents the area using the width at surface level. These values are normalized by the contact area according to the nanoindentation hardness. A horizontal line $A_S/A_I = 1$ depicts the case of equivalent scratch and nanoindentation hardness. Each datapoint is the average of at least 60 measurements.



Fig. C4. (a) Application of the Nix-Gao model for wear experiments performed using 5 μ m tip on aluminum (AI) and copper (Cu). The scratch hardness values are normalized by a resulting macroscopic scratch hardness. (b) Application of the Nix-Gao-type model for wear experiments performed using 5 μ m tip on soda-lime glass (SLG), cementite (Fe₃C), and silicon (Si). Each datapoint is the average of at least 9000 measurements.

Matorial	$E_{\rm ex}$ (mN) $H(h)$ (GPa)	$H_S(w_{surface})$	$H_{S}(w_{pile-up})$	$H_{S}(w_{max.slope})$	
Wateria	P_N (IIIIN)	$\Pi_{S}(n_{c})$ (GF a)	(GPa)	(GPa)	(GPa)
	5	7.09	-	-	-
	10	9.74	-	-	-
Fe₃C	20	11.84	11.24	5.88	10.05
	50	14.10	15.15	9.06	12.21
	100	14.82	15.16	9.34	12.55
	5	3.98	-	-	-
Soda-	10	5.06	-	-	-
lime	20	6.28	-	-	-
glass	50	8.06	-	-	-
	100	9.35	-	-	-
	5	8.71	-	-	-
Si	10	10.36	-	-	-
	20	11.84	-	-	-
	50	14.57	-	-	-
	100	16.38	-	-	-
	5	2.10	1.93	0.85	1.57
	10	1.99	2.31	1.25	2.08
Cu	20	1.95	2.25	1.30	1.85
	50	1.59	1.37	0.85	1.08
	100	1.59	1.63	0.73	1.24
	5	0.86	0.78	0.40	0.52
AI	10	0.55	0.36	0.24	0.30
	20	0.51	0.41	0.23	0.32
	50	0.48	0.48	0.31	0.43
	100	0.44	0.30	0.25	0.29

Table C1: Average scratch hardness H_S for wear experiments conducted using 5 um tip.

Material	F _N	$H_S(h_c)$	$H_S(w_{surface})$	$H_{S}(w_{pile-up})$	$H_{S}(w_{max.slope})$
Matorial	(mN)	(GPa)	(GPa)	(GPa)	(GPa)
Fe₃C	10	3.21	-	-	-
	20	3.91	-	-	-
	50	4.84	-	-	-
	100	6.16	-	-	-
	200	7.41	-	-	-
	10	1.89	-	-	-
Soda lime	20	2.35	-	-	-
dlass	50	3.16	-	-	-
	100	3.95	-	-	-
	200	4.82	-	-	-
	10	3.37	-	-	-
	20	3.81	-	-	-
Si	50	4.91	-	-	-
	100	6.10	-	-	-
	200	7.47	-	-	-
	10	1.23	1.13	0.53	0.75
	20	1.34	1.11	0.65	0.82
Cu	50	1.31	1.09	0.70	0.86
	100	1.18	1.29	0.73	0.98
	200	1.14	1.25	0.69	1.00
	10	0.71	0.52	0.29	0.37
	20	0.69	0.58	0.35	0.42
AI	50	0.65	0.61	0.32	0.43
	100	0.35	0.36	0.19	0.22
	200	0.35	0.43	0.16	0.25

Table C2: Average scratch hardness H_S for wear experiments conducted using 20 um tip.

Material	Fe	e₃C	ļ A	A
<i>F_N</i> (mN)	10	100	10	100
$H_{S}(h_{c})$ (GPa)	9.7	14.8	0.55	0.44
RSD $H_S(h_c)$ (%)	6.4	0.7	6	3.9
$H_{S}(w_{pile-up})$ (GPa)	-	9.34	0.21	0.25
$RSDH_{S}(w_{pile-up})(\%)$	-	6.5	4.5	5.9
Percent difference between $H_S(h_c)$ and $H_S(w_{pile-up})$ (%)	-	45.4	78.5	55.1
Percent difference between $H_S(h_c)$ for 10 and 100 mN (%)	4	1.6	22	2.2
Percent difference between $H_S(w_{pile-up})$ for 10 and 100 mN (%)		-	17	7.4

Table C3. Relative standard deviation (RSD) for the $H_S(h_c)$ and $H_S(w_{pile-up})$ hardness values in cementite (Fe₃C) and aluminum (AI) obtained using 5 µm tip with 10 and 100 mN normal force.

Material	Fe₃C		AI	
<i>F_N</i> (mN)	10	100	10	100
$H_{S}(h_{c})$ (GPa)	3.2	6.2	0.74	0.35
RSD $H_S(h_c)$ (%)	8.1	0.5	6.4	2.3
$H_S(w_{pile-up})$ (GPa)	-	-	0.29	0.19
RSD $H_S(w_{pile-up})(\%)$	-	-	9.7	5
Percent difference between $H_S(h_c)$ and $H_S(w_{pile-up})$ (%)	-	-	87.4	59.3
Percent difference between $H_S(h_c)$ for 10 and 100 mN (%)	63.8		79.2	
Percent difference between $H_S(w_{pile-up})$ for 10 and 100 mN (%)		-	41	.7

Table C4. Relative standard deviation (RSD) for the $H_S(h_c)$ and $H_S(w_{pile-})$ hardness values in cementite (Fe₃C) and aluminum (AI) obtained using 20 µm tip with 10 and 100 mN normal force.

Material	F_N (mN)	$A_{S}(h_{c})/A_{I}$	$A_{S}(w_{pile-up})$
	5	1.56	-
	10	1.14	-
Fe₃C	20	0.93	1.89
	50	0.78	1.22
	100	0.74	1.19
	5	1.47	-
	10	1.16	-
Soda-lime glass	20	0.93	-
	50	0.73	-
	100	0.63	-
	5	1.37	-
	10	1.15	-
Si	20	1.01	-
	50	0.82	-
	100	0.73	-
	5	0.21	0.56
	10	0.22	0.35
Cu	20	0.23	0.34
	50	0.28	0.52
	100	0.28	0.60
	5	0.25	0.53
	10	0.39	0.9
AI	20	0.42	0.94
	50	0.45	0.71
	100	0.49	0.88

Table C5: Contact area ratio $A_S(h_c)/A_I$ for wear experiments conducted using 5 um tip.

Material	<i>F_N</i> (mN)	$A_{S}(h_{c})/A_{I}$	$A_S(w_{pile-up})/A_I$
	10	3.45	-
	20	2.84	-
Fe₃C	50	2.29	-
	100	1.80	-
	200	1.50	-
	10	3.11	-
	20	2.50	-
Soda-lime glass	50	1.86	-
	100	1.49	-
	200	1.22	-
	10	3.54	-
	20	3.14	-
Si	50	2.43	-
	100	1.96	-
	200	1.60	-
	10	0.36	0.82
	20	0.33	0.67
Cu	50	0.34	0.63
	100	0.37	0.60
	200	0.38	0.64
	10	0.30	0.74
	20	0.31	0.62
AI	50	0.33	0.67
	100	0.61	1.13
	200	0.62	1.34

Table C6: Contact area ratio $A_S(h_c)/A_I$ for scratch experiments conducted using 20 um tip.

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09/2012 – 06/2016	Bachelor's degree in Applied Mechanics National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" (Ukraine)
09/2002 – 05/2012	Secondary education at Gymnasium "Consul" No. 86 (Ukraine)

RESEARCH ACTIVITY AND INTERNSHIPS

02/2018 – 07/2018	Research assistant
	Otto-von-Guericke Universität Magdeburg, Institute of Mobile Systems (Germany)
12/2016 – 06/2017	Research assistant
	Otto-von-Guericke Universitat Magdeburg, Institute of Process Engineering (Germany)
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	Internship Program of German Business for Ukraine
OTHER ACTIVITY	

12/2019 – 05/2021	Internal PhD Representative
	Max-Planck-Institut für Eisenforschung (Germany)

PUBLICATIONS

First author publications

2022	Tsybenko, H.; Tian, C.; Rau, J.; Breitbach, B.; Schreiber, P.; Greiner, C.; Dehm, G.; Brinckmann, S.: Deformation and phase transformation in polycrystalline cementite (Fe ₃ C) during single- and multi-pass sliding wear. In Acta Materialia 227, p. 117694., 2022.
2021	Tsybenko, H.; Farzam, F.; Dehm, G.; Brinckmann, S.: Scratch hardness at a small scale: Experimental methods and correlation to nanoindentation hardness. In Tribology International 163, p. 107168, 2021.
2020	Tsybenko, H.; Xia, W.; Dehm, G.; Brinckmann, S.: On the commensuration of plastic plowing at the microscale. In Tribology International 151, p. 106477, 2020.

Co-author publications

2022	Bishara, H.; Tsybenko, H.; Nandy, S.; Muhammad, Q. K.; Frömling, T.; Fang, X.; Best, J. P.; Dehm, G.: Dislocation- enhanced electrical conductivity in rutile TiO2 accessed by room-temperature nanoindentation. In Scripta Materialia 212, p. 114543, 2022.
2021	Fang, X; Bishara, H.; Ding, K.; Tsybenko, H.; Porz, L.; Höfling, M., Bruder, E.; Li, Y.; Dehm, G.; Durst, K.: Nanoindentation pop-in in oxides at room temperature: Dislocation activation or crack formation? In J American Ceramic Society 104 (9), pp. 4728–4741, 2021
2019	Kauss, O.; Tsybenko, H.; Naumenko, K.; Hütter, S.; Krüger, M.: Structural analysis of gas turbine blades made of Mo-Si-B under transient thermo-mechanical loads. In Computational Materials Science 165, pp. 129–136, 2019.

CONFERENCES AND WORKSHOPS

2021	Tsybenko, H.; Dehm, G.; Brinckmann, S.: Deformation and chemical evolution in cementite (Fe ₃ C) during small-scale tribology. Oral presentation at European Congress and Exhibition on Advanced Materials and Processes - EUROMAT, Virtual, 2021
2021	Tsybenko, H.; Dehm, G.; Brinckmann, S.: Scratch hardness at a small scale: experimental methods and correlations with nanoindentation hardness. Oral presentation at Vienna Virtual Materials Tribology Workshop, ViViMaT, Virtual, 2021
2020	Tsybenko, H.; Dehm, G.; Brinckmann, S.: Deformation and chemical evolution during tribology in cementite. Oral presentation at Materials Science and Engineering Congress (MSE), Virtual, Darmstadt, Germany, 2020
2020	Tsybenko, H.; Xia, W.; Dehm, G.; Brinckmann, S.: On the commensuration of plastic plowing at the microscale. Poster presentation at Nanobrücken 2020: Nanomechanical Testing Conference & Bruker User Meeting, Düsseldorf, Germany, 2020

2019 Tsybenko, H.; Brinckmann, S.; Dehm, G.: Deformation of pearlitic steels during nanotribology. Poster presentation at 46th Leeds-Lyon Symposium on Tribology, Lyon, France, 2019

Neuss, 15/08/2022