

Understanding thermophysical properties across length-scales: A study on metallic materials

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Nomenclature

Symbols

α_{th}	Coefficient of thermal expansion	K^{-1}
a	Thermal diffusivity	$m\ s^{-2}$
$a_{lattice}$	Lattice parameter	nm
A	Surface	m^2
B	Factor of angular dependence of ferromagnetic resonance field	T
c_p	Specific heat capacity	$J\ (kg\ K)^{-1}$
C_V	Isochoric heat capacity	$J\ kg^{-1}$
CuK_α	Characteristic α spectral line of Copper	$\text{\AA}$
CuK_β	Characteristic β spectral line of Copper	$\text{\AA}$
d	Grain size	m
D_{10}	Max. size of the smallest 10% of particles	m
D_{50}	Median particle size	m
D_{90}	Max. size of the smallest 90% of particles	m
δH	External magnetic field strength	T
ϵ	Porosity	
η	Efficiency	
f	Microwave modulation frequency	Hz
g	Gyromagnetic factor	
$g_{ }$	Gyromagnetic factor parallel to the sample plane	
$g_{\perp}$	Gyromagnetic factor perpendicular to the sample plane	
G_a	Weight force in air	N
G_l	Weight force in liquid	N
H	Biot number	
H_0	External magnetic field strength	T
H_{FMR}	Ferromagnetic resonance strength	T

H_{res}	Resonance field strength	T
H_m	Microwave modulation amplitude	T
I	Current	A
J	Bessel function	
L	Thickness	m
L_0	Lorenz number	$W \Omega K^{-2}$
M	Magnetization	$A m^{-1}$
n	Coefficient of shape anisotropy	$J m^{-3}$
N	Number of spins	
p	Pressure	Pa
P_{mw}	Microwave field power	W
$\dot{Q}$	Heat flux	W
ρ	Density	$kg m^{-3}$
ρ_{el}	Resistivity	Ωm
ρ_l	Density of the liquid	$kg m^{-3}$
ρ_{RT}	Density at room temperature	$kg m^{-3}$
ρ_{powder}	Powder density	$kg m^{-3}$
ρ_{solid}	Solid density	$kg m^{-3}$
R	Resistance	Ω
σ	Electrical conductivity	$S m^{-1}$
S	Seebeck coefficient	$V K^{-1}$
$t_{1/2}$	Time to reach half of the maximum temperature	s
T	Temperature	K
T_0	Reference temperature	K
T_C	Curie temperature	K
Θ	Angle of the magnetic field	rad
U	Internal energy	J
U_{el}	Voltage	V
U_T	Thermal voltage	V
V	Volume	m^3
λ	Thermal conductivity	$W (m K)^{-1}$
$\bar{\lambda}$	Mean thermal conductivity	$W (m K)^{-1}$
$\lambda_{electronic}$	Electronic thermal conductivity	$W (m K)^{-1}$
$\lambda_{magnonic}$	Magnonic thermal conductivity	$W (m K)^{-1}$
$\lambda_{phononic}$	Phononic thermal conductivity	$W (m K)^{-1}$
$\lambda_{resulting}$	Resulting thermal conductivity	$W (m K)^{-1}$
γ_L	Lorentz factor	

ν	Microwave frequency	Hz
ω_{mw}	Microwave angular frequency	s ⁻¹

Abbreviations

3D	Three-dimensional
A	Anisotropy field
Al ₂ O ₃	Aluminium oxide
AM	Additive manufacturing
ASTM	American Society for Testing and Materials
at. %	Atom-%
bcc	Body-centered cubic
BSE	Backscattering electrons
CAD	Computer aided design
CCA	Compositionally complex alloys
CESR	Conduction electron spin resonance
CTE	Coefficient of thermal expansion
D(EF)	Electron state density at the Fermi surface
DIN	Deutsches Institut für Normung
DOS	Density of states
DSC	Differential Scanning Calorimetry
EDS	Energy-dispersive spectrometry
ESR	Electron spin resonance
FE	Finite elements
FEA	Finite element analysis
fcc	Face-centered cubic
HEA	High-Entropy Alloy
ISO	International Organization for Standardization
LFA	Laser flash analysis
LWT	Chair of Materials Technology
MEA	Medium-Entropy Alloy
MgO	Magnesium oxide
OES	Optical emission spectrometry
PC	Paramagnetic cluster

PBF-LB/M	Powder bed fusion by laser beam melting of metals
PSD	Particle size distribution
RD	Rolling direction
RT	Room temperature
SEM	Scanning electron microscopy
SiC	Silicon carbide
SRO	Short-range ordering
TD	Transversal direction
wt. %	Weight-%
XRD	X-Ray diffraction

Chapter 1

Introduction and technological background

1.1. Motivation: Understanding thermophysical properties

The various influences on the thermophysical properties of materials constitute a fascinating research area that is gaining increasing significance in science and technology. The term "thermophysical properties" refers to several parameters, including thermal conductivity. These parameters comprise density, coefficient of thermal expansion (CTE), thermal conductivity, thermal diffusivity, specific heat capacity, as well as electrical conductivity and the Seebeck coefficient. Among these properties, the thermal conductivity, as a central thermophysical parameter, plays a pivotal role in numerous industrial applications and scientific disciplines. A precise understanding of these properties at the microscopic level is crucial, as it not only affects the efficiency of heat exchange processes but is also fundamental for the development of innovative materials in fields such as energy, transportation, and manufacturing. This work is therefore dedicated to the comprehensive examination and analysis of diverse factors across different length-scales influencing thermophysical properties, contributing to an enhanced understanding of these essential material characteristics.

As an example, when it comes to heat engines, the efficiency η has to be maximized for economical and environmental reasons [1, 2]. The loss of efficiency results from entropy, which is correlated with the inefficiency of a system [3]. Within an closed

system, entropy can only rise, leading to an energy loss in the thermal process. In a conversion process that operates with a cold and a hot reservoir, with temperatures T_{Cold} and T_{Hot} , respectively, e.g. the idealized Carnot-cycle, the highest achievable efficiency η is described by Eq. 1.1 [1, 3].

$$\eta = \frac{W}{Q} = 1 - \frac{T_{Cold}}{T_{Hot}} \quad (1.1)$$

According to Eq. 1.1, a high efficiency comes from significant differences between hot and cold reservoirs, showing that T_{Hot} has to be increased and T_{Cold} has to be lowered. Since the temperatures occurring in the process depend significantly on the capabilities of the materials used, optimization of their properties is of fundamental importance for the development of new and optimization of existing processes. In gas turbines, for example, the heat must be dissipated from the material in order to prevent damage to the material. By enhancing the intrinsic properties of the used materials, cooling is easier to achieve within the given turbine design.

In addition to heat engines, energy efficiency optimization potentials can also be found in industrial applications such as the tooling industry, particularly in fields like steels for press hardening. By controlling the process temperatures, processing times can be reduced, output enhanced, and quality improved [4]. Therefore, the development of materials with a tuned thermal conductivity can significantly reveal possibilities to increase cost to profit ratios and furthermore reduce environmental impact due to increased energy efficiency. Since the need for optimized thermophysical properties is critical, research regarding the fundamental understanding of the underlying principles becomes evident. Nevertheless, thermal conductivity embodies a fundamental physical principle in the context of heat transfer, making this parameter inherently complex. Following, a description of the fundamentals will be given to describe the complexity and underline the necessity of intensive research.

1.2. Fundamentals of heat transfer

Thermodynamically, heat is defined as energy, elucidating the process through which thermal energy moves through a material. The principle of heat conduction is rooted in the temperature disparities between two mass points. This difference in energy initiates

a transfer of heat or energy from the warmer to the colder mass point, indicating an exchange of energy. Heat can not only be transferred by conduction, but also convection and radiation, which both describe different heat transfer modes [5]. Firstly, heat convection is a mode of heat transfer that occurs through the movement of fluid (liquid or gas). It involves the transfer of heat energy from one region to another through the actual movement of the fluid [5]. This movement can be natural, driven by density differences caused by temperature variations, or forced, induced by external factors like a fan or pump. In contrast, radiation is a mode of heat transfer that does not require a medium and can therefore occur in a vacuum [5]. It involves the emission, transmission, and absorption of electromagnetic waves.

Nevertheless, when it comes to heat transfer in solid materials, the above-mentioned mechanisms, convection and radiation, become less relevant, making heat conduction the outstanding parameter in this case. The ability to conduct heat is described as thermal conductivity, which indicates how well a material can transfer or conduct heat [6]. Higher thermal conductivities, therefore, indicate a highly efficient heat transfer possibility within the solid. Accordingly, the term "transfer" induces a transport of energy inside of a material. In metallic solids, this transport is not achieved by the exchange of matter but through lattice vibrations and electrons, within their nature as charge carriers and cause of magnetism [7]. Resulting from these forms of transport, three quantum particles can be identified that enable heat transfer in metallic materials and determine their potential of thermal conductivity accordingly: phonons, electrons and magnons [7, 8]. Nevertheless, in metallic materials, the magnonic contribution can be disregarded since it is notably small [9]. By addition of the electronic $\lambda_{\text{electronic}}$ and phononic $\lambda_{\text{phononic}}$ contributions, the overall thermal conductivity $\lambda_{\text{resulting}}$ can be calculated according to Eq. 1.2 [9].

$$\lambda_{\text{resulting}} = \lambda_{\text{electronic}} + \lambda_{\text{phononic}} \quad (1.2)$$

Subsequently, both electronic and phononic thermal conductivity are of particular interest when it comes to the overall thermal conductivity of metallic materials and technical alloys. Within the formulation given in Eq. 1.2, the phononic contribution describes the conduction of energy through the metallic lattice. Consequently, the metallic lattice and its resulting properties on the atomic scale are of extensive importance regarding the transfer of heat and a short description of the metallic bonding mechanism becomes necessary, as its characteristics are determining both electronic

and phononic thermal conductivity, as it is a direct result of the electronic state of the atoms.

As the bonding of atoms is dependent on the number of electrons on the outer orbital, so called valence electrons, a differentiation can be made between covalent, ionic and metallic bonding. All atoms tend to form a stable electronic configuration by filling their outer orbital with eight electrons. In ionic bonds, the total number of valence electrons from all participating atoms adds up to eight. The bonding is then achieved by the lower-valence atom donating its valence electrons to the higher-valence atom. As a result, all atoms achieve fully filled outer orbitals, giving the atoms a stable electronic configuration. If the number of valence electrons can not be added up to eight, a covalent bond can be established by forming a binding electron pair [10]. Nonetheless, only four or less electrons can be shared between the binding atoms, making this form of bonding impossible for atoms with less than four valence electrons. Therefore, an electron cloud is formed, which consists of all valence electrons of the atoms that take part in the metallic bonding [10, 11]. Within this form of bonding, the atoms are now positively charged, leading to a repelling force between each other, which is counteracted with the negative charge and corresponding bonding force effected by the electron cloud. Throughout this repelling force, short- and long-distance ordering of the atoms occurs [10].

Phononic heat transfer

As already mentioned, the heat transfer through the metallic lattice is referred to as phononic heat transfer. Within this physical principle, heat is transferred through the binding of the atoms. The phononic heat transport results from a heat gradient inside of the lattice, leading to a potential energy. As the system minimizes its energy, a lattice vibration results from the equalizing temperatures [8]. The quasiparticle resulting from this lattice vibration are called phonons, which transmit their energy through elastic impacts [8, 10]. Further, the number of phonons is dependent on the temperature, with low temperatures ($T < 100$ K) leading to a low concentration of phonons and therefore low chance of elastic impacts, resulting in a high phononic thermal conductivity [8]. Accordingly, with rising temperature an increased concentration of phonons becomes evident, leading to a higher chance of elastic impacts that lowers the phononic thermal conductivity. This phenomenon is described as phonon-phonon scattering in particular. Besides, other defects of the crystal lattice, such as vacancies, also lead to scattering

and decrease the phononic thermal conductivity [12, 13].

Electronic heat transfer

Since the metallic lattice results from the metallic bonding of materials with four or fewer valence electrons, an electron cloud is formed, which serves to bind the atomic nuclei [10]. Within this metallic bonding, many electrons are participating in the electron cloud. Speaking about a single atom, electrons occupy a discrete energy level. Since many electrons are present due to the bonding character and a high number of participating atoms, electrons have to occupy a higher energetic state than in a single atom, leading to the formation of energy bands. Accordingly, the two relevant energy bands in metallic materials are the valence and the conduction band [10]. Following, only electrons in a higher energetic state than the valence band can contribute to thermal and electrical conduction. These electrons are called free or conduction electrons and are located in the conduction band, that can also be vacant [10]. As only the free electrons are mobile and able to transport energy, the ability of a metal to conduct current is correlated with the concentration of free electrons [10]. In insulating and semiconductive materials, there exists an energy gap between the valence band and the conduction band, known as the bandgap. This gap arises from the quantum mechanical properties of electrons and has a specific width. Corresponding to a significantly broad bandgap, the ability to conduct electricity can be disabled up to the melting point, making the material a good insulator at any temperature. Materials with a smaller bandgap can therefore conduct current according to the given temperature [10]. Accordingly, valence and conduction band overlap partly in conducting materials like metals and enable the flow of current. Through thermal activation, electrons can be detached from the valence band and even overcome the bandgap, making them part of the conduction band, further increasing the electrical conductivity [10].

Given that the number of free electrons is of significant interest for the thermal conductivity of a metal, the material specific Fermi energy becomes relevant as it determines the electronic state of a material [10]. At a temperature of 0 K, a limiting energy, the so-called the Fermi energy, exists, below which all energy levels are occupied by electrons according to the Pauli principle. Above this specific energy at 0 K, electrons do not occupy any energy levels [11]. As the temperature increases, electrons can occupy energy levels above the Fermi energy. Consequently, the number of free electrons depends on the specific Fermi energy and the temperature [8]. In a manner similar to

phononic heat transport, an energy difference arises in electrons due to a temperature gradient, which is equalized by the movement of free electrons [11, 14]. Therefore, a connection between electrical conductivity and electronic heat conduction, resulting in electronic thermal conductivity, can be made. This relationship is described by the Wiedemann-Franz law [15, 16] as follows:

$$\lambda_{\text{electronic}} = T \cdot \sigma (L_0 - S^2) \quad (1.3)$$

Within the Wiedemann-Franz law (Eq. 1.3), the electronic thermal conductivity $\lambda_{\text{electronic}}$ can be calculated with the electrical conductivity σ , the Seebeck coefficient S , and the Lorenz number L_0 . The Lorenz number has been firstly determined by *Drude* [17] and refined by *Sommerfeld* [18] and is calculated to be $L_0 \approx 2.44 \text{ W}\Omega\text{K}^{-2}$. Additionally, the temperature T also influences the electronic and overall thermal conductivity.

Overview on scattering effects in metallic materials and technical alloys

The aforementioned temperature dependency of electronic thermal conductivity results from scattering effects caused by electron-phonon collisions, which have an increased probability as temperature rises. Scattering decreases both electrical and thermal conductivity since the carriers of heat conduction lose their energy and therefore cannot compensate for energy differences resulting from temperature gradients. These scattering effects can occur across all length-scales, from electron-phonon, phonon-phonon or electron-electron interactions or lattice distortions [12] up to scattering at dislocations [19], grain boundaries [20–22], or precipitates [23]. Consequently, a brief description of the relevant mechanisms for this work will be provided, starting with a metallic crystal lattice without defects where only electron and phonon interactions occur, up to the more complex multiphase alloys.

Beginning with electron-phonon scattering, the probability of these effects depends on the velocity of electrons and the number of phonons, both of which increase with rising temperature [8, 11]. Concerning the temperature-dependent influence of electron-electron interactions, this scattering effect can only be observed at temperatures lower than 4 K and can therefore be neglected in this work [8, 11]. Nonetheless, electron-phonon scattering is of significant interest as it shows pronounced influences on the

overall energy transport mechanisms, especially at higher temperatures [8]. During electron-phonon scattering, the electron loses a part of its energy, and a phonon is absorbed or created as the lattice vibration changes [8]. This particular scattering is highly effective and can lead to significant decreases in thermal conductivity [8]. Additionally, electrons can be scattered by other electrons through magnetic effects resulting from their magnetic moment, with spin-up and spin-down characteristics, particularly in ferromagnetic materials, depending on both the material and the temperature [8]. At higher temperatures, phonon-phonon scattering also becomes relevant. This scattering effect is proportional to temperature, crystal structure, and atomic mass [8].

Additionally, scattering of phonons and electrons can occur at defects in the crystal lattice, vacancies, dislocations, phase and grain boundaries, and precipitates [24]. The influence of impurities and alloying elements is particularly significant, as they have a pronounced effect on the thermal conductivity of metallic materials. Starting with electrons, this effect arises from the different Coulomb potential between the alloying element and the free electron [8]. Consequently, a local magnetic field emerges, reducing the velocity of the electrons and thus decreasing both electrical conductivity and electronic thermal conductivity [8, 25]. Regarding phonon scattering at these point defects, such as alloying elements, it results from local distortions due to mass differences between lattice and alloying atoms. Therefore, the mass and volume of the alloying element determine the extent of the scattering [26, 27].

Dislocations also serve as scattering sites for both phonons and electrons, with high complexity due to their effects resulting from inhomogeneously induced stress fields [28–30]. Specifically, the type of dislocation—whether edge or screw dislocation—as well as the dislocation density, are of major importance [29, 30]. Furthermore, grain boundary scattering is relevant for both electronic and phononic thermal conductivity. The impact of grain boundaries relies mainly on grain size, carrier concentration, and dielectric constant [31]. However, these effects influence the phononic considerably less than to the electronic thermal conductivity [32, 33]. Moreover, lattice distortions are also of high importance regarding the scattering effects of carriers, as these distortions are characterized by a high dislocation density which leads to a decrease in thermal conductivity [19, 23, 34].

Moreover, the multiphase nature of many materials can further increase the complexity of scattering effects. In multiphase alloys, the overall thermal conductivity can be influenced by the thermal conductivity of the present phases, their geometry and distribution, and the interfacial thermal resistance [35]. For instance, when precipitates exhibit a lower thermal conductivity than the surrounding matrix, their presence is

significantly impacting the thermophysical properties of the material [7, 36, 37]. Additionally, the geometry of these precipitates further complicates the overall thermal conductivity, creating complex pathways for heat flux. Therefore, all aspects of matrix and precipitate have to be taken into account when it comes to the overall thermal conductivity of multiphase alloys.

As a result, all types of crystal lattice defects lead to scattering, thereby decreasing the thermal conductivity of metallic materials. The intricate interplay of these effects makes the thermophysical properties highly complex and warrants thorough investigation due to their challenging nature.

1.3. Measurement principles

1.3.1. Electron spin resonance

The electronic configuration is crucial for determining the thermophysical properties, as it relates to the number of conduction electrons, which fundamentally dictate the electronic thermal conductivity. A method commonly referred to in materials science for analyzing the electronic state of a metallic sample is Electron Spin Resonance (ESR) [38, 39]. ESR is a spectroscopic measurement principle that exploits magnetic resonance to detect transitions between different energy levels of a system of weakly coupled magnetic moments of electrons in an external magnetic field [40]. By analyzing the ESR spectrum, information about the electronic environment, local magnetic fields, and the interactions of unpaired electrons with their surroundings can be obtained, providing insights into the electronic structure and properties of the material. Initially, all electrons have a spin, generating a magnetic moment characterized by the Bohr magneton and the gyromagnetic or Landé factor (g -factor or g -value) [41]. When two electrons are paired, one electron has a spin-up and the other a spin-down, leading to the neutralization of the total moment. When a sample containing paramagnetic species is exposed to a constant magnetic field and perpendicularly irradiated with microwaves, the unpaired electrons can transition between spin states, absorbing energy at specific resonance frequencies [40]. As this consumes energy, a specific signal, followed by the resonance, is measured and displayed in the ESR spectrum. This resonance condition occurs when the energy difference between the spin states matches the energy of the microwave photons [40, 41].

In terms of experimental measurement, an oscillating field of microwaves is required to induce dipole transitions between different energetic states. The power of these microwaves is proportional to the number of quanta absorbed and their energy [40]. Accordingly, three relevant magnetic fields are applied to the sample, all perpendicular to one another: a magnetic field composed of a constant field and a modulation field, namely a high-frequency microwave field, and a reinforcement magnetic field [41]. Typically, the microwave field is held constant at a frequency of typically 9-9.5 GHz, while the magnetic field is varied [40]. The detector current is measured in accordance with the field strength of the modulated field, which is then amplified for further analysis. Regarding the measurement signal, the aforementioned specific dipole transitions are experimentally broadened by various dynamic effects, such as spin relaxation, or static effects, such as inhomogeneities. As a result, the dipole transitions do not appear as sharp resonance lines in the observed spectrum. An example of a characteristic ESR spectrum is shown in Fig. 1.1, which illustrates the absorption of a specific transition.

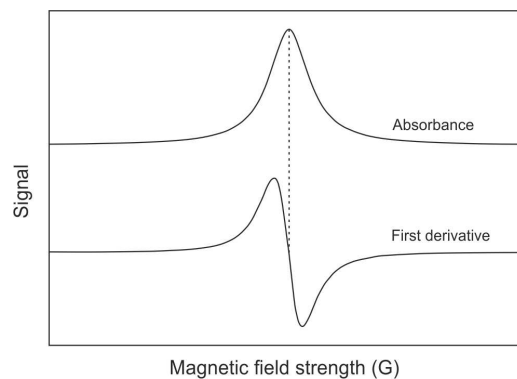


Figure 1.1.: Schematic ESR spectrum.

1.3.2. Measurement of thermophysical properties

When measuring thermophysical properties, two main principles are distinguished: stationary and dynamic measurement [9, 42]. In stationary measurements, thermal conductivity is directly assessed by placing a sample between a heat source and a heat sink, allowing heat to flow along the sample axis from hot to cold. The thermal conductivity can be calculated using the general, one dimensional Fourier's law (Eq. 1.4) [9, 42].

$$\bar{\lambda} = -\frac{\dot{Q}}{A} \cdot \frac{\Delta x}{\Delta T} \quad (1.4)$$

In Eq. 1.4, $\bar{\lambda}$ represents the mean thermal conductivity, $\dot{Q}$ describes the heat flux, A the cross-sectional area, Δx the distance, and ΔT the temperature difference. When only minor temperature differences are applied, the mean thermal conductivity $\bar{\lambda}$ is approximately equal to the actual thermal conductivity λ [42].

For more detailed insights into the influencing factors of individual materials, the dynamic measurement principle becomes favorable. This approach is based on the separate and temperature-dependent measurement of the density ρ , thermal diffusivity a , and specific heat capacity c_p [42]. The dynamic measurement principle offers several advantages. By isolating each component, it allows for a more comprehensive understanding of how each factor contributes to the overall thermal conductivity, especially when it comes to their temperature dependent behavior. Following, the thermal conductivity λ can be calculated using Eq. 1.5 by employing the density $\rho(T)$, thermal diffusivity $a(T)$, and specific heat capacity $c_p(T)$.

$$\lambda(T) = \rho(T) \cdot a(T) \cdot c_p(T) \quad (1.5)$$

Since each of these parameters is measured individually and temperature dependent according to the dynamic measurement principle, it is possible to quantify the influence of various factors, such as the microstructure of metallic materials, separately, and independently on each individual parameter. As this work aims to understand the thermophysical properties at different length-scales and draw corresponding conclusions, this is of particular relevance. However, since each factor requires individual measurement, the fundamentals of the measurement methods will be briefly explained.

Density

Generally speaking, density describes the ratio of mass to volume. However, due to the challenges associated with accurately measuring the geometry of various sample bodies, density measurement often relies on Archimedes' principle at room temperature, which utilizes the buoyant force. According to the Archimedes' principle, a body

experiences a counterforce to the gravitational force, the so-called buoyant force, when it is immersed in a liquid. This buoyant force is equal to the gravitational force of the displaced liquid [43]. Accordingly, the weight force of the sample differs when measured in air and in liquid. With a negligible density of air, the density of a sample at RT can be calculated according to Eq. 1.6 [43].

$$\rho_{RT} = \frac{G_a}{G_a - G_l} \cdot \rho_l \quad (1.6)$$

Within Eq. 1.6, ρ_{RT} is the density of the sample at RT, G_a is the weight force of the sample in air, G_l is the weight force of the sample in liquid, and ρ_l is the known density of the liquid.

As already mentioned, the density is the ratio of mass to volume, which leads to microstructural influences on the density through the atomic configuration [44]. Therefore, the lattice structure, the lattice parameter $a_{lattice}$, and the atomic weight are relevant when it comes to the determination of the density of an alloy. Following, an alloying with atoms with an increased atomic weight can possibly lead to a higher overall density, if the lattice parameter is only changed insignificantly. Accordingly, phase transformations like fcc to bcc transitions also lead to changes in the density, which are due to significant differences in the packing density [24, 44].

In this work, not only the various influences on the thermophysical properties along length-scales are studied, but also the temperature dependency plays a crucial role. Therefore, the density has to be measured as a function of the temperature. The temperature dependent density can be calculated by using the coefficient of thermal expansion (CTE) α_{th} , which is measurable through dilatometry. By employing Eq. 1.7, the temperature dependent density can be calculated.

$$\rho = \frac{\rho_{RT}}{1 + 3 \cdot \alpha_{th}(T - T_0)} \quad (1.7)$$

In 1.7, ρ is the temperature-dependent density, ρ_{RT} is the density at room temperature (RT), α_{th} describes the CTE, T_0 is the initial temperature at which ρ_{RT} was measured, and T is the corresponding temperature.

As previously described, density is the ratio of mass to volume. As the temperature rises, the lattice expands while the atomic mass remains constant, resulting in an increase in volume and a corresponding decrease in density. The lattice expansion

resulting from a temperature increase is a result of atomic interactions, specifically attractive and repulsive forces between atoms. On the one hand, the binding force between atoms leads to an attractive force between the atoms. On the other hand, the repulsive force results from the positive atomic charge and the temperature dependent vibration of the atoms. With rising temperature, the vibration increases, leading to an increase of the lattice parameter through extended distances between the atoms and therefore general expansion of the crystal lattice [11, 44].

Thermal diffusivity

The thermal diffusivity a is of particular interest when it comes to the transport properties of metallic materials, as it describes the time-temperature dependent characteristics of a material. Based on the fundamentals of heat transfer, thermal diffusivity describes the rate at which heat is conducted through a material [45]. Nevertheless, the measurement of the thermal diffusivity possesses some difficulties and can therefore only be assessed indirectly by measuring time-temperature profiles. For solid materials, the laser flash analysis (LFA) is referred to as the most appropriate technique to measure thermal diffusivity [9]. By means of LFA, a heat source, a laser in this particular case, heats a sample from one side, while the time-temperature profile is measured at the other side of the sample. This procedure is shown in Fig. 1.2a.

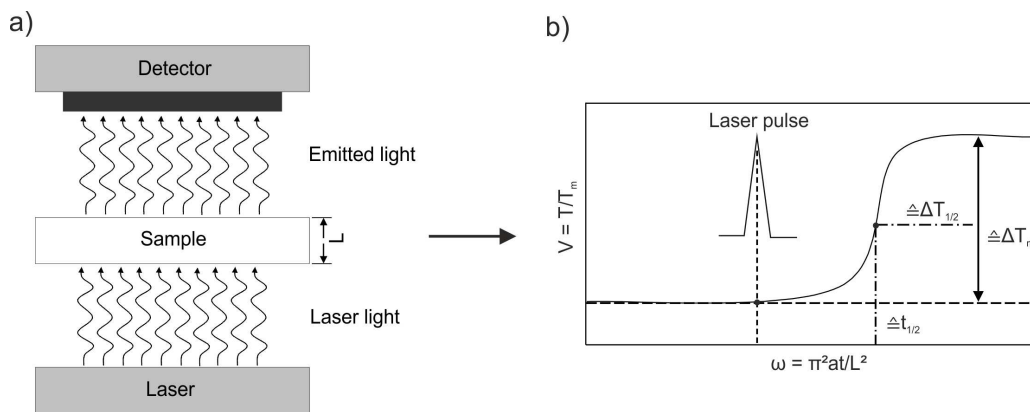


Figure 1.2.: Schematic diagram of the laser flash principle.

The LFA is based on the work by *Parker et al.* [46], which assumes a one-dimensional,

stationary heat transfer. Given an thermally insulated solid of uniform thickness L , the temperature-time distribution $T(x, t)$ can be described according to Eq. 1.8 [46].

$$T(x, t) = \frac{1}{L} \int_L^0 T(x, 0) dx + \frac{2}{L} \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \pi^2 a t}{L^2}\right) \cos\left(\frac{n \pi x}{L}\right) \int_L^0 T(x, 0) \cos\left(\frac{n \pi x}{L}\right) dx \quad (1.8)$$

Within Eq. 1.8, a describes the thermal diffusivity, t the time, and n representing the integer indexing the terms in the infinite series, therefore the number of oscillations, and controlling the frequency and amplitude of each harmonic mode. By using a pulse with a instantaneously heat pulse which is uniformly absorbed within a infinitesimal small depth at the front surface and the two dimensionless parameters $V(L, t) = T(L, t)/T_M$ and , and $\omega = \pi^2 a t / L^2$, with T_M being the maximum temperature at the rear surface where $x = L$, these simplifications yield Eq. 1.9. For a more detailed step-by-step simplification, the reader is encouraged to consult Ref. [46].

$$V = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \omega) \quad (1.9)$$

The curve of Eq. 1.9 is shown in Fig. 1.2b. Using V equal to 0.5, which equals to the $t_{1/2}$ -time, ω equals 1.38, enabling a calculation of the thermal diffusivity a according to Eq. 1.10 [46].

$$a = 1.38 \cdot \frac{L^2}{\pi^2 \cdot t_{1/2}} \quad (1.10)$$

The $t_{1/2}$ time is characterized as the necessary time for the sample surface reaching half the maximum temperature ΔT_m , as described by $\Delta T_{1/2}$ in Fig. 1.2b.

However, the simplification of the previously mentioned equations refers to an adiabatic state with an infinite heat source [47–49]. Additionally, deviations to the model occur in very thin samples and multi-layer material measurements [50, 51]. Since these boundary conditions are not achievable in technical applications, signals from laser flash measurements will differ from the theoretic model. For this reason, optimization

procedures are carried out on the mathematical formulation of the fit of the measured values in order to mathematically eliminate these influences. Several solutions have been developed to correct the heat loss of the sample due to the non-adiabatic state of the measurement [49, 52–54] and to take into account the time profile of the laser pulse [55–57]. Nevertheless, the challenge of a simultaneous presence of heat loss and a finite laser pulse still remains as well as a decision as to when which correction has to be applied [58]. Therefore, new formulations had to be found that take both effects into account. Commonly used is the combined model by *Dusza* [58], which was also applied in this work. Implementing the known laser pulse function $f(t)$ into the heat loss function by *Cape and Lehmann* [47] yields Eq. 1.11 [58].

$$T(x = L, r = 0, t) = \sum_{n=1}^{\infty} C_n \xi_n \sum_{m=1}^{\infty} D_i(H_1) \exp\left(\frac{\omega_{m,n} t}{t_c}\right) P\left(\frac{\omega_{m,n}}{t_c}, t\right) \quad (1.11)$$

In Eq. 1.11, dimensionless parameters C_n , ξ_n , $D_i(H_1)$, t_c , and $\omega_{m,n}$ are employed, which are calculated as follows (Eq. 1.12–1.15) [58]. Additionally, the pulse coefficients of the laser beam $P(\omega_{m,n}/t_c, t)$ is known, as the pulse form is given by the experiment.

$$C_n = \frac{(-1)^n 2\xi_n}{\xi_n^2 + 2H_2 + H_2^2} \quad (1.12)$$

$$D_i(H_1) = \frac{2H_1}{H_1^2 + \lambda_1^2} \frac{1}{J_0(k_i)} \quad (1.13)$$

$$t_c = \frac{L^2}{\pi^2 a} \quad (1.14)$$

$$\omega_{m,n} = -\frac{L^2}{\pi} \left(\frac{\xi^2}{L^2} + \frac{k_i^2}{R_s^2} \right) \quad (1.15)$$

Accordingly, H_1 is the Biot number at the lateral surface, H_2 the Biot number at the front surface, a is the thermal diffusivity, and k_i is the solution to the equation $H_1 J_0(k_i) = k_i J_1(k_i)$, with J_0 and J_1 being the Bessel functions of zero and first degree. Additionally, the dimensionless parameter ξ_n can be calculated by solving $(\xi_n^2 - H_2) \tan(\xi_n) = 2\xi_n H_2$. As there are three unknown variables thermal diffusivity a , H_1 , and H_2 , a non-linear parameter estimation is carried out by fitting the numerical calculation to the existing measurement. Therefore, both finite pulse and heat loss are considered, enabling also the measurement of multi-layer materials or porous

materials, which have a high degree of heat loss during the measurement.

Specific heat capacity

Generally speaking, heat capacity is the ratio of heat input to the temperature change of a system [59]. When it comes to the measurement of the specific heat capacity of a metallic material, the approximation of the measurement as a closed system is accurate, with the metallic sample being the closed systems. Accordingly, the system has an internal energy U , which is changed through heat supply or dissipation. As no mechanical energy is exchanged between sample and surrounding and the volume stays constant, the isochoric heat capacity can be defined (Eq. 1.16) [10, 59].

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (1.16)$$

As a constant volume is not achievable in metallic materials with rising temperature, a constant pressure can be assumed, making the usage of the enthalpy H necessary, which is dependent on the internal Energy U , pressure p , and volume V (Eq. 1.17) [10].

$$H = U + p \cdot V \quad (1.17)$$

Assuming isobaric changes and a specific consideration with the mass m , a formulation of the specific heat capacity c_p is found, which uses a partial derivation of the enthalpy to the temperature [10] (Eq. 1.18).

$$c_p = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_p \quad (1.18)$$

Similar to the overall thermal conductivity, the specific heat capacity is also a composition of various contributions, which also influence each other [11]. Analogous to thermal conductivity, the specific heat capacity is consequently made up of contribu-

tions from the lattice vibration and electrons, which can be characterized in different components. The contribution of the lattice vibration can thus be split in a harmonic and anharmonic contribution. The harmonic contribution describes only the phononic contribution without any interactions and depends on the material specific Debye temperature [11]. The Debye temperature T_D is the temperature, at which all possible phononic states are occupied, meaning that according to the Debye model a temperature increase above T_D will not lead to an increasing isochoric heat capacity [11]. Since phonons also interact with each other, this must also be taken into account. This is done by means of the anharmonic component, which is particularly relevant for higher temperatures. Additionally, there is a contribution of dilatation, which is caused by the difference between isobaric and isochoric specific heat capacity [11]. Additionally, the electron gas also has a temperature-dependent internal energy and therefore heat capacity. An increase in internal energy through a heat supply comes from rise in kinetic energy of the electron gas [11]. Nevertheless, this contribution is insignificant at RT in comparison to the lattice and magnetic heat capacity [8]. This is due to the nature of phonons and electrons. As phonons are quasiparticles, they have zero mass at rest, allowing them to be formed and annihilated, when in comparison in electrons the particle number conservation applies and they are subject to the Pauli principle [11]. Further, the magnetic contribution is induced by the electron spin and particularly influenced by the crystal lattice [11]. As this contribution is difficult to determine, an indirect calculation by subtracting the harmonic, anharmonic and electronic parts from the specific heat capacity is carried out [60].

Most common is the determination of the specific heat capacity by differential scanning calorimetry (DSC), which is based on the differential measurement of a sample and a reference, enabling the calculation of heat fluxes (Fig. 1.3).

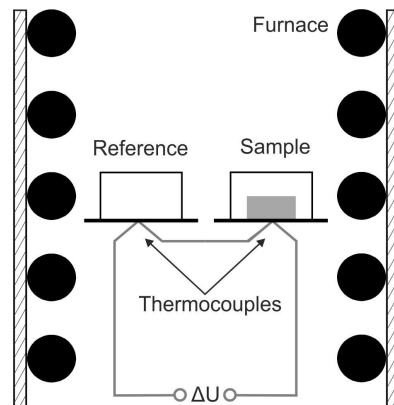


Figure 1.3.: Schematic diagram of a DSC.

In this work, a heat flux DSC will be used, which relies on the measurement on the differential heat flux which is dependent on the calibration with a known material and a temperature difference between sample and reference [61]. As the furnace is heated, differences in temperature between sample and reference is achieved, which correlates with the heat capacity of the material. Within this principle, three steps are carried out: Baseline measurement, calibration, and sample measurement. A baseline measurement is carried out at first, with just empty crucibles placed on reference and sample position, leading to the measurement of the error due to the inevitable condition that both positions have the same temperature. Following, a baseline is measured, which is used to correct both calibration and sample measurement. Afterwards, the calibration measurement uses a reference sample (e. g. sapphire) with has a known specific heat capacity, enabling the calculation of a calibration parameter k . Lastly, the material of interest can be measured. The specific heat capacity of that sample can then be calculated with the calibration parameter and the heating rate according to Eq. 1.19 [61].

$$c_p = k \cdot \frac{\dot{Q}_s - \dot{Q}_r}{m \cdot \dot{T}} \quad (1.19)$$

According to Eq. 1.19, the specific heat capacity c_p can be calculated with the calibration constant k , the heat flux at the sample $\dot{Q}_s$ and at the reference $\dot{Q}_r$, the sample mass m , and the mean heating rate $\dot{T}$. As all three measurements – reference, calibration, and sample measurement – require ideally equal boundary conditions, the heating rate, gas and pressure, crucible and crucible position should not be changed by any means while measuring [61].

Electronic thermal conductivity

According to Eq. 1.3, a measurement of the electrical conductivity σ and the Seebeck coefficient S is necessary to compute the electronic thermal conductivity. Therefore, a measurement of these two parameters has to be carried out prior to the calculation. As the electrical conductivity σ is the reciprocal value of resistivity ρ_{el} , the resistivity is measured as it is easily accessible. The measurement of the resistivity is based on Ohm's law, which is used to calculate the general resistance R and is given in Eq. 1.20 [62].

$$R = \frac{U_{el}}{I} \quad (1.20)$$

Accordingly, the resistance R is calculated by the ratio of voltage U_{el} to current I . As the resistance R is generally influenced by the dimensions of the sample, a specific resistance, the resistivity ρ , is used (Eq. 1.21) [62].

$$\rho_{el} = R \cdot \frac{A}{L} \quad (1.21)$$

With the knowledge of the surface area A , the sample height L , and the resistance R , the resistivity ρ_{el} can be calculated. Commonly used is the four-wire measurement method, which reduces influences of wire and connection influences [62].

As stated above, the Seebeck coefficient S has to be measured. The Seebeck coefficient is a consequence of thermoelectricity, in which a voltage arises due to an electric field, induced by a thermal gradient. Following, this is a direct result of the electronic thermal conductivity. The Seebeck coefficient S is temperature and material-specific and measured according to Eq. 1.22 [63].

$$U_T = \int_{T_2}^{T_1} S(T) dT \quad (1.22)$$

In this equation, U_T describes the voltage due to the thermal gradient between T_1 and T_2 . Consequently, the Seebeck coefficient can be measured directly by means of a fairly low temperature gradient and the measurement of the occurring voltage. For this reason, Seebeck coefficient and resistivity are usually measured hand-in-hand in one apparatus.

1.4. State of the art and need for research

Due to their possible benefits in technical applications and given high complexity, thermophysical properties of diverse materials are of significant interest in research

and technology. In this work, three influences on the thermophysical properties will be of special interest:

- Influence of chemical composition and electronic configuration on thermophysical properties of single-phase, complex alloys
- Resulting influences of microstructure on the thermophysical properties in multicomponent, multiphase alloys
- Heat conduction in powder beds in additive manufacturing processes

Following, the importance of the thermophysical properties in these fields will be elaborated. In the first step, the intrinsic influences of the metal lattice on the thermophysical properties will be considered. Building on this, the complexity of the influences on the thermal conductivity of metallic materials rises, as different length-scales cause different thermophysical behavior. With ascending length scale, the complexity increases as the fundamental influences due to crystallographic defects and electronic and phononic density of states will also be present in alloys with multiphase microstructures. Lastly, those influences will be examined in the context of powder beds. In powder beds, it is crucial to understand how much the thermal conductivity of the solid phase contributes to the overall thermal conductivity of the bulk and to what extent the thermal resistance between the powder particles affects the overall thermal conductivity.

Following, this work seeks to make a contribution to the comprehension of thermophysical properties in relation to fundamental solid state physics, microscopic and mesoscopic physical attributes. A thorough analysis is attained by examining the thermal conductivity of metallic materials in depth. As already mentioned, the thermal conductivity λ is composed of three distinct components: density ρ , thermal diffusivity a , and specific heat capacity c_p , which are then used to calculate the thermal conductivity according to Eq. 1.5. Although each of these components depends on the temperature, they are physically independent, showing the necessity to investigate each factor individually and as a function of temperature. Additionally to the dynamic measurement of the thermal conductivity, a breakdown into phononic and electronic contributions will be carried out individually to enable a more detailed investigation. Accordingly, this work is split into three sections. At first, various materials with a single-phase lattice structure are examined with respect to their different chemical

composition and corresponding lattice structure. In the next step, tool steels will be examined, whereby the influence of their multiphase nature and lattice distortions is of considerable relevance here. The last step is the examination of powders, where the relationship between intrinsic and extrinsic influencing factors on the thermophysical properties will be investigated. In this specific case, the influence of microstructure is of high relevance, as it is not considered in the scientific literature up to now. Accordingly, influences of the contact resistance between powder particles might also influence the thermophysical properties. A overview of the research presented here is given in Fig. 1.4. A brief introduction to each topic according to the relevant length scale and the individual need for research is pointed out in the following.

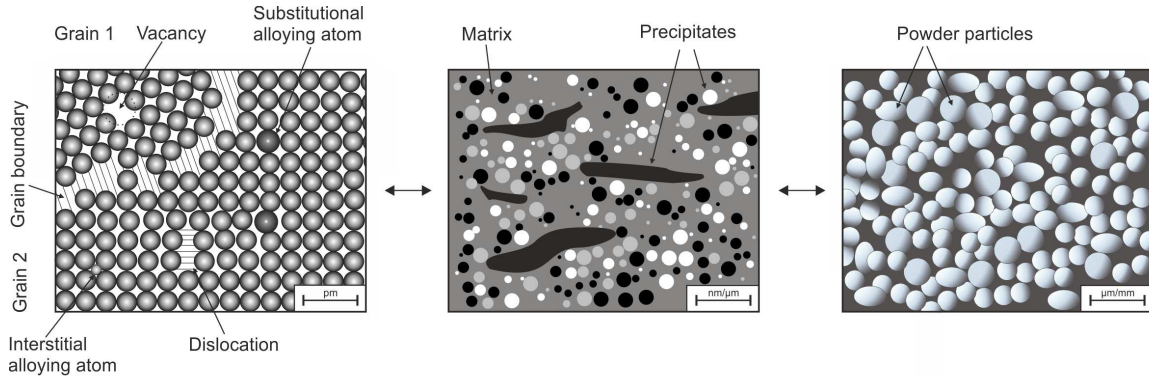


Figure 1.4.: Overview on the different length-scales investigated in this work.

1.4.1. Fundamental influences on the thermal conductivity

The thermophysical properties of metallic materials are complex and not easy to comprehend through mere common sense, making an independent insight on the influential factors necessary. In detail, a basic knowledge about the fundamental physical properties of the crystal lattice is essential, especially when it comes to the relationship between thermal conductivity and microstructure. As already mentioned, two fundamental transport mechanisms of heat - phononic and electronic - are determinant for the thermophysical properties. The mechanisms are closely related and therefore influence one-another. Fundamental knowledge about the physical electronic properties is therefore crucial for understanding the thermophysical properties of any alloys. To establish a solid foundation, it is advisable to initially investigate single-phase materials. This approach allows isolating the influence of individual elements on thermophysical

properties. By varying only this input variable, the underlying mechanisms can be better understood.

Building up on this guiding concept, the investigation of single-phase materials is fundamental. One particularly interesting group of single-phase metallic materials are High- and Medium-Entropy Alloys (HEA and MEA). HEA and MEA are one group of compositionally complex alloys (CCA) with promising properties as functional and structural materials [64–67]. The group of HEA and MEA is characterized by consisting of two to four (MEA) or five or more (HEA) elements in a near-equiatomic configuration. CCAs are recognized in recent publications as model alloys, as their properties stem from chemical complexity and exhibit a high degree of variation with alterations in chemical composition. For example, these alloys exhibit substantial potential in electronical applications [68, 69] or show significant improvement when it comes to mechanical properties [70–74]. The capacity for those use-cases lies within the possibility to customize these properties by tuning chemical compositions. For this reason, CCAs are exceptionally well-suited for the research presented here, as they can effectively contribute to understanding the influence of chemical composition on electron configuration and thermophysical properties. Nevertheless, in the past years, research regarding CCAs has been done mostly in fields of mechanical properties [70–76]. However, there exists a growing recognition of the need to explore and understand the electronic and thermophysical aspects of CCAs [77, 78].

According to the aforementioned principle regarding the breakdown of complexity of the thermophysical properties, the correlation between thermophysical properties and chemical composition has to be outlined by investigating the electronic configuration of these alloys experimentally. The investigations regarding the measurement of the electronic configuration and, in particular, the number of free electrons has mostly been addressed in the field of carbon and nitrogen (C+N) alloyed austenitic stainless steels. Mostly used for these studies is the conduction electron spin resonance (CESR) measurement technique, which has its foundation on the ESR technique and is used for the determination of the number of conduction electrons [38]. For example, through CESR measurements, a strong correlation between interstitial alloying and density of free electrons with correlations with mechanical properties could be found [38, 39, 79–81]. Especially alloying with N led to a significantly increased amount of free electrons, influencing the mechanical properties beneficially. As already mentioned, by means of CCAs such differences in electronic structures are also expected due to changes in chemical compositions, making the measurement of the electronic configuration highly beneficial in the understanding of the properties of the novel group of metallic materials.

Additionally, a comprehensive investigation about the individual factors yielding the thermal conductivity is still lacking, showing a research gap in the understanding of the various influences of thermophysical properties of CCAs. Even though the specific heat capacity has been investigated by means of differential scanning calorimetry (DSC) for many CCAs to investigate phase transitions, the thermal diffusivity has not been investigated thoroughly. Problematically, the thermal diffusivity is of special interest as it is known to significantly impact the thermophysical properties of metallic materials and is effected by numerous factors such as phonon-electron interactions and other scattering effects. These influences are exclusively observable through this parameter. Therefore, specifically investigating thermal diffusivity is one of the main goals of the research regarding CCAs. Furthermore, the correlation between electronic configuration and atomic bonding will be investigated carefully in order to understand the fundamental influences on thermophysical properties of CCAs. Throughout the analysis of single-phase CCAs, the fundamental influences on the thermophysical properties can be understood in detail.

1.4.2. Influence of multiphase microstructure and lattice distortions

As already mentioned, it has been shown that the thermal conductivity depends on numerous factors that are challenging to comprehend. Significant influences in alloys can result from temperature, alloying, lattice distortions of the matrix, and precipitates which lead to different scattering effects on different length-scales. Accordingly, the complexity of the thermophysical properties increases when lattice distortions and precipitates are present in an alloy. A commonly used group of alloys, which can be used to analyze the aforementioned influences, are Fe-based tool steels.

Specifically in tool steels, the most pronounced influence on the thermal conductivity arises from alloying elements, as they lead to a significant scattering of heat carriers. Nevertheless, alloying is crucial in tool steels, as it determines other technological properties like hardness and can significantly improve wear resistance. Alloying is generally necessary for both martensitic hardening and the formation of precipitates, which are both highly relevant for tool steels as they determine their technological performance. Nevertheless, both of these mechanisms decrease thermal conductivity, but in a different manner. With regard to alloying, carbon is of paramount importance, as it is only through the introduction of carbon that martensitic hardening can be achieved,

leading to severe lattice distortions. Solely carbon alloying can significantly reduce the thermal conductivity of a material. However, the use of martensitic hardening in tool steels will further reduce the thermal conductivity. Another prominent example of the influence of alloying is Cr, another extremely relevant element when it comes to tool steels, which is also known to reduce thermal conductivity [82].

As already mentioned, martensitic hardening is crucial for tool steels. Nevertheless, within martensitic hardening, a considerable dislocation density is observed. This dislocation density exerts a notable influence on thermal conductivity within this specific microstructural framework. *Wilzer et al.* [23] demonstrated that inducing a dislocation density in pure Fe, comparable to that in martensite, reduces the phononic density of states. Consequently, the harmonic contribution to specific heat is altered, leading to a diminished phononic thermal conductivity within the lattice.

Additionally, in the context of multiphase alloys and tool steels in particular, the presence of precipitates must be taken into account. Within tool steels, tempering carbides stand out as a crucial group, contributing to increased hardness and wear resistance. Nonetheless, carbides and other precipitates can be disadvantageous for a high thermal conductivity, as their thermal conductivity differs significantly from the matrix thermal conductivity [36, 37, 83]. Therefore, the geometry and distribution of those carbides is of exceptional relevance regarding the overall thermal conductivity of these alloys. Consequently, reductions in thermal conductivity arise from scattering effects in the matrix and the scattering effects through carbides.

Additionally to the scientific interest, thermophysical properties are not only of great interest in research but also exert a significant influence on the performance of tool steels in technical applications. Particularly, the steel and tool industry holds significant potential regarding these properties, as the majority of technical processes can be substantially optimized by adjusting the thermophysical properties of the alloys employed. One of the processes where the thermophysical properties of tools have a considerable impact on time, cost, and quality and have been extensively investigated is press-hardening. Given that the costs of the produced parts are generally highly dependent on the efficiency of press hardening, there is a significant interest in optimizing and maximizing the thermal conductivity of the utilized tool steel [23, 84, 85]. In other technological domains, the thermal conductivity of tool steel significantly impacts the quality, efficiency, and costs of processes such as die-casting aluminum components or polymer processing [4, 86, 87]. All of these applications have a common need for tool cooling. When a material with high thermal conductivity and similarities in other technological properties, like tensile strength and hardness, is employed, there is an overall improvement in performance. Consequently, the economic efficiency of the whole man-

ufacturing process is significantly enhanced by employing materials with an improved thermal conductivity.

In contrast to CCAs, the influences on the thermophysical properties of tool steels have been extensively investigated in the past. However, forecasting the thermal conductivity of such complex systems is challenging, especially when considering the manufacturing process. Since tools exhibit different microstructures depending on their production, variations in thermophysical properties are anticipated. These differences are not easily comprehensible and require thorough research. On one hand, individual factors based on the dynamic measurement principle must be taken into account. On the other hand, lattice distortions and the chemical composition of the matrix and hard phases, as well as their geometry and distribution are known to influence thermal conductivity. Consequently, quantification within each specific tool is necessary. By comparing different tool steels made from different materials in different production processes and featuring distinct microstructures, predictions about performance in technical applications can be formulated. This approach allows for the development of a favourable carbide alignment and enhances understanding in comparison to existing tools, showing the necessity of thermophysical properties in technical applications.

1.4.3. Thermophysical properties of powder beds

The first two central research topics focus mainly on the intrinsic influences on the thermophysical properties of solid metallic materials. Given that these influences fundamentally rely on heat transfer in a solid, it becomes essential to understand how the heat conduction of a bulk, consisting of powder and the surrounding gas, is affected by the thermal conductivity of the powder particles. Following, the aforementioned analysis of the thermophysical properties of a solid material enables a detailed analysis of the extrinsic factors influencing the thermophysical properties of a bulk. Accordingly, influences on the thermal conductivity of a bulk can result from extrinsic factors like the surrounding gas as well as the contact resistance between powder particles, showing the necessity of further research.

Additionally, bulks of metallic powder are of high interest regarding the recent technological research as they are often used in additive manufacturing (AM) technologies. The field of AM has been gaining serious interest in research and technology in the past years, since it enables a high freedom in design and facilitates time and resource efficiency to produce highly customized parts [88–90]. When it comes to the AM through

powder materials, some challenges become visible that hinder the productivity of the AM-process and the quality of the build parts. The challenges of the process arise from uncertainties, such as those resulting from the kinematic movement of the melt, absorbability of the laser, distortion due to thermal gradients, and phase transformations in the cooling phase of the part [91–95]. In all the aforementioned uncertainties, one common and significant variable prevails: the thermal conductivity of the bulk, consisting of powder and the surrounding gas, giving this topic an even higher relevance [94].

Analytical solutions to the heat conduction problem in powder beds were proposed as early as the 1960s from, for example, *Masamune and Smith* [96] and validated through early transient-hot bridge approaches. Problems in the early analytical solutions for the heat conduction models occur from the importance of enclosed gas, differing particle sizes, surface roughness and therefore contacts between the particles. Therefore, refinements of the analytical solutions have then been carried out by *Lambert and Fletcher* [97] and *Gusarov and Kovalev* [98]. The early laser flash applications also exhibited major inaccuracies, showing the necessity for modern techniques [6]. A recent study from *Rombouts et al.* [99] gives far more insight inside of the thermophysical properties of a powder by analysing the thermal diffusivity of a bulk and giving analytical reasons for the measured values. Problematically, all these studies consider only ideal powder beds consisting of particles with the same diameter, providing insufficient details about the actual heat conduction occurring in a PBF-LB/M process.

Due to the recent development of AM techniques like PBF-LB/M, a higher interest in maximizing economical outcome of the process has to be achieved. Therefore, there is an interest in utilizing beds with a broad particle size distribution (PSD) and allowing for a wider variation in chemical composition. By this, waste is reduced as the atomization processes utilized in research and industry produces a wide range of particle geometry. As a result, the particles deviate significantly from each other in terms of both shape and size. Hence, real powder beds show differences from the idealized powders that have been considered in the past analytical solutions, leading to experimental approaches regarding the heat flux problem in powder beds.

Nevertheless, in the recent past, efforts have been made to measure real powders intended for the PBF-LB/M process to gain insights into the actual heat distributions occurring during the building process. Together, they employ the laser flash technique, enabling the indirect measurement of thermal conductivity [100, 101]. Due to the measurement principle, the laser flash measurement seems inapplicable for the determination of powder properties. The difficulties arise, for example, from the challenging determination of the geometry of the powder bed, which significantly determines the

thermal conductivity. These challenges were addressed through the implementation of holders or containers, aiming to provide a more controlled environment for the powder bed, thereby mitigating the difficulties that were previously mentioned. Decisive advancements in the measurement of thermophysical properties were achieved by *Ahsan et al.* [102], *Zhang et al.* [103], and *Cheng et al.* [104]. All of these investigations employed powder-filled capsules, with the latter mentioned produced in-situ by PBF-LB/M. All of these experimental approaches had uncertainties in common, which resulted from heat transfer between capsule and powder, signals from the capsule, and other influences that were complex to address. Consequently, the thermal conductivity of a filled capsule itself was measured, and individual parameters were determined through simulations. Accordingly, challenges arise from the necessity to optimize numerous unknowns and accept the heating of the powder, where the occurrence of sinter necks and other thermal effects in the powder can pose difficulties.

Therefore, a necessity to directly determine the thermophysical properties of the powder without subsequent simulation or other influences results, in order to gain a detailed insight into the underlying principles of heat conduction in the powder bed. Based on these results, it is then possible to better understand the heat distribution during the PBF-LB/M process, enabling more accurate predictions of the phases and microstructures that will occur in the subsequent simulation of the process. By enabling the simulation of the final component, it becomes possible to optimize subsequent heat treatments or predict the properties.

When it comes to powder beds and their thermophysical properties, the specific factor influencing the overall thermal conductivity remains ambiguous. Both thermal diffusivity and specific heat capacity could be of particular interest, as the density is contingent on factors such as porosity, solid or ideal density, and the thermal expansion of the solid. Conversely, the correlation between specific heat capacity and thermal diffusivity of powders and their corresponding solids is not well-understood. Additionally, the temperature dependency of specific heat capacity and thermal diffusivity poses a challenge. The behaviour of powders might exhibit a similar temperature dependency as their corresponding solids, with sintering effects potentially introducing unexpected thermophysical properties. Accordingly, there are several questions that have to be answered to obtain a fundamental understanding of the thermal conductivity of a bulk. With this knowledge, a comprehensive understanding about the heat distribution inside AM-Processes can be gained. In further steps, a forecast about the resulting phases and corresponding microstructure with resulting properties becomes possible. Nevertheless, in the context of an holistic approach informations about the thermophysical properties of the solid phases and a comprehensive analysis of the

properties is necessary.

1.5. Publications and procedure

This work presents three individual peer-reviewed publications which represent the authors original work. All three papers have already been published and are reproduced here with minor editorial changes for improved readability. The three chapters in the core of this these are represented by the publications, which are in this order:

1. Berger, A.; Benito, S.; Konchits, A.; Laplanche, G.; Shanina, B.; Weber, S.: "*Thermophysical properties of equiatomic CrMnFeCoNi, CrFeCoNi, CrCoNi, and CrFeNi high- and medium-entropy alloys*", in *Materials Today Communications* (2024)
2. Berger, A.; Benito, S.; Kronenberg, P.; Weber, S.: "*Impact of Thermophysical Properties of High-Alloy Tool Steels on Their Performance in Re-Purposing Applications*", in *Materials* (2022), 15(23), 8702
3. Berger, A.; Ziesing, U.; Benito, S.; Weber, S.: "*Experimental determination of the high-temperature thermal conductivity of steel powders*", in *Powder Technology* 431 (2024), p. 11902

Within these publications, the research objectives outlined in Section 1.4 will be addressed. The first publication focuses on the investigation of single-phase CCAs, whose unique nature allows for an in-depth analysis of the underlying influences on thermophysical properties. This study was conceptualized and written by the author of this work, who also conducted the thermophysical measurements and metallographic characterizations. ESR characterizations were performed by A. Konchits and B. Shanina from the V. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine. G. Laplanche helped source the specimens for the measurement campaigns. S. Benito, G. Laplanche, and S. Weber supervised the study and contributed to reviewing and editing the publication.

The second publication shifts focus to multiphase alloys, specifically tool steels, to evaluate the impact of secondary phases on thermophysical properties. Similar to the

first study, the author of this work conceptualized, wrote, and conducted the investigations. P. Kronenberg helped source the specimens for the measurement campaigns. P. Kronenberg, S. Benito, and S. Weber contributed to reviewing and editing, with S. Benito and S. Weber also supervising the research.

The third publication examines the thermophysical properties of powders to identify both intrinsic and extrinsic influences on bulk heat conduction. The author of this work designed a powder capsule for measuring the thermophysical properties of powder and performed the thermophysical measurements on both solid and powder and metallographic investigations on the solid materials. Bulk density and particle size distribution measurements, as well as metallographic investigations of the powder materials, were conducted by U. Ziesing. The investigated materials were commercially produced and bought from the individual supplier. U. Ziesing, S. Benito, and S. Weber contributed to reviewing and editing the publication, with S. Benito and S. Weber also providing supervision.

Chapter 2

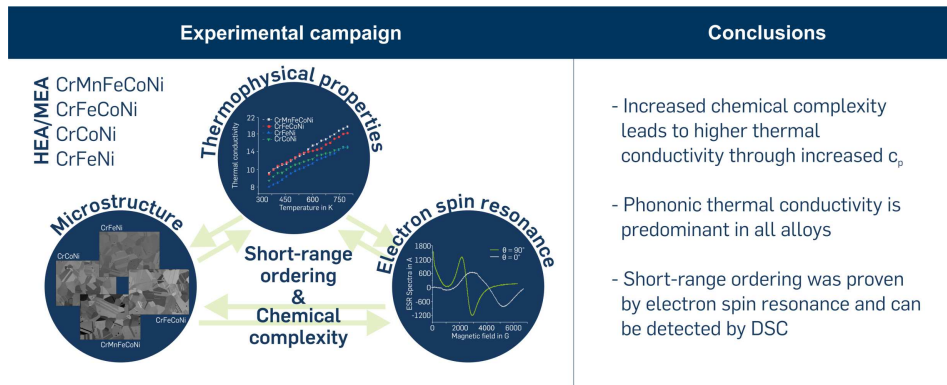
Thermophysical properties of equiatomic CrMnFeCoNi, CrFeCoNi, CrCoNi, and CrFeNi high- and medium-entropy alloys

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Abstract

High- and medium-entropy alloys have emerged as promising materials with significant potential for diverse technical applications. Notably, their use in the field of energy technology has attracted particular interest, where thermophysical properties play a pivotal role. In this context, this study aims to investigate the thermophysical properties, namely thermal expansion behavior, thermal diffusivity, specific heat capacity, thermal conductivity, and the electric resistivity of single-phase face-centered cubic alloys between 300 K and 773 K. In addition to thermal conductivity, the electric resistivity was measured. Based on the Wiedemann-Franz law, electronic and phononic contributions to the overall thermal conductivity were evaluated. Complementary insights into the electronic state of the investigated materials were obtained by electron spin resonance measurements, revealing the presence of short-range ordering in all alloys. The specific heat capacity is found to dominate the thermal conductivity. Furthermore, the study shows the decisive influence of chemical complexity on the thermophysical properties. Notably, the observed influences extend to the electronic thermal conductivity, pointing out the correlation between composition and heat transport properties. This comprehensive investigation provides a foundation for understanding and tailoring the thermophysical behavior of the studied alloys, offering valuable insights for their targeted deployment in advanced energy applications.

2.1. Introduction

The design and in-depth exploration of multifunctional materials based on the metallic d-block elements represent an advancing field within materials science. Among the

various multicomponent systems, so-called compositionally complex alloys (CCAs) are currently acknowledged as a promising category of functional or structural materials [64–67]. In comparison with conventional alloys, CCAs break down the traditional notions, since they consist of two to four principal elements (Medium Entropy Alloys – MEA) or five or more elements (High Entropy Alloys – HEA) in near-equiatomic configuration [105, 106] and are currently recognized as a promising category of functional and/or structural materials. These materials exhibit substantial potential and exceptional performance in terms of mechanical properties [70–76], electronic applications [68, 69], corrosion resistance [107–110], and irradiation resistance [111, 112]. Furthermore, HEAs and MEAs show high potential for applications in renewable energy [113] and energy storage, like hydrogen retention [114, 115] or oxygen evolution and reduction [116].

The equiatomic single-phase fcc CrMnFeCoNi HEA, commonly known as the ‘Cantor alloy’ [64] and its derived variants are often acknowledged as suitable single-phase model systems due to their different high-entropy effects resulting from their chemical complexity and are thus frequently proposed for these use cases. An important feature of this innovative class of alloys is its ability to offer new ways of tailoring material properties by manipulating compositional complexity. This involves alterations in the variety and concentration of elements [74]. In addition, it not only expands the conventional concept of alloying and microstructure modification but also presents challenges in understanding physical properties and the potential for tuning them. The extensive potential of these alloys underlines therefore the desirability of acquiring knowledge regarding their thermophysical properties in a broad temperature range. This is particularly noteworthy considering the abundance of literature on the mechanical properties, creating a knowledge gap regarding the thermophysical characteristics.

The thermophysical properties of HEAs, including thermal conductivity, specific heat capacity, density, thermal diffusivity and coefficient of thermal expansion (CTE) as well as the resistivity and the Seebeck coefficient, are pivotal in understanding their behavior under diverse temperature conditions in applications like catalysis [117] or energy conversion [118]. The knowledge about the influences on these specific properties is the key to optimizing HEAs for specific applications, from advanced engineering materials to sustainable energy solutions. Moreover, the study of their thermophysical properties challenges our fundamental understanding of materials science, providing insights into the intricate interplay between composition, microstructure, and physical properties. Within the last decade, relevant contributions have been made by *Jin et al.* [77, 119], who used experimental and first-principle approaches to determine the thermophysical properties of Ni-containing HEAs and MEAs. They found that the

influence of Cr is critical and dramatically reduces the thermal conductivity of the alloys, while other studies focused mainly on the influence of Al in these alloys [120]. When it comes to thermophysical properties, the influence of electrons and short-range ordering (SRO) may be significant, as suggested by first-principle simulations [77, 119]. However, the experimental verification of the electronic state, which is predominant for the determination of thermophysical properties, remains elusive. In previous works, measurements of the electronic state have primarily been performed using conduction electron spin resonance (CESR), a method that can be used to determine the quantity of free electrons [38, 39, 81]. Additionally, the effects of atomic ordering and bonding are measurable within this principle. This approach was particularly focused on steels and is extended in the present study to encompass HEAs and MEAs. To sum up, the here presented experimental study focuses on both the measurement of thermophysical properties between 300 K and 773 K and the determination of the electronic state of HEAs and MEAs.

2.2. Methods

2.2.1. Materials preparation and heat treatment

Equiatomic and single-phase fcc alloys including CrMnFeCoNi, CrFeCoNi, CrCoNi and CrFeNi were produced from high-purity raw elements (≥ 99.9 wt.%). The latter were vacuum induction melted under a protective Ar atmosphere as 2.1 kg ingots using a Leybold Heraeus IS 1/III vacuum induction furnace, poured into a cylindrical steel mold (45 mm diameter, 160 mm height), and cooled to 300 K as described in one of our previous studies [121]. Subsequently, the cast ingots underwent turning on a lathe, reducing their diameter to 40 mm, after which they were cut into two equal halves (each 80 mm in height) perpendicular to the rod axis. The cast ingots were homogenized at 1473 K for 48 hours in evacuated fused silica tubes (3×10^{-5} mbar), cold worked by rotary swaging at 300 K with a diameter reduction of $\approx 60\%$ using a four-die rotary swaging machine (HMP R6-4-120-21S, HMP Umformtechnik GmbH), and recrystallized at 1100 °C for 30 min, see Ref. [122] for more details.

2.2.2. Metallographic preparation, microstructural analysis, and chemical composition

Specimens were ground using silicon carbide abrasive papers down to 600 mesh (corresponding to a particle size of $9\text{ }\mu\text{m}$). Subsequently, the specimens underwent polishing by diamond suspension subsequently to $1\text{ }\mu\text{m}$. The final polishing step was executed using a vibropolishing machine (Buehler Vibromet 2) with colloidal silica (particle size of $0.06\text{ }\mu\text{m}$) over a two-day period. Phase characterization was conducted using X-ray diffraction (XRD) after heat treatment and subsequent thermophysical measurements, performed on the samples utilized for DSC measurements. XRD was performed using a Bruker D8 Advance. CuK_α radiations ($\text{CuK}_{\alpha 1} = 1.54060\text{ }\text{\AA}$, $\text{CuK}_{\alpha 2} = 1.544392\text{ }\text{\AA}$) were utilized, with an operating voltage of 40 kV and an operating current of 40 mA. A Lynx-Eye detector, a detector divergence slit, a 30° -to- 90° 2θ range, a 0.01° step size, and a 10-second measurement time per step were employed. To suppress CuK_β radiation, a Ni-filter was used. Line-profile Rietveld analyses using the software MAUD (University of Trento) have been performed to obtain the lattice parameters of the investigated alloys [123].

Microstructural analyses were performed through scanning electron microscopy (SEM). Backscattered electron (BSE) micrographs were employed using a MIRA3 SEM by TESCAN ORSAY HOLDING, a. s.. Grain size analysis was conducted using four BSE micrographs taken at various locations spaced several millimeters apart, spanning from the center to the outer surface of the recrystallized rods. The Heyn linear intercept method was employed to determine the average grain size. Eight lines of equal length were superimposed on each micrograph, in line with the guidelines outlined in ASTM E-112 [124]. Each line was required to intersect a minimum of 50 grains, resulting in a substantial number of intercepts, typically ranging from 500 to 1000 per micrograph. To calculate the average grain size, four independent measurements were carried out, and the error bars reflect the mean deviation from the calculated mean value.

The chemical compositions of the alloys were analyzed using energy dispersive spectrometry (EDS). EDS was applied using an X-MaxN 50 detector by Oxford Instruments with an acceleration voltage of 15 keV at a working distance of 15 mm. Additionally, oxygen and nitrogen contents were determined through carrier gas hot extraction with a ONH2000 by ELTRA GmbH.

2.2.3. Thermophysical properties

Thermal conductivity

The thermal conductivity λ was assessed using the dynamic indirect measurement method, in which the specific heat capacity c_p , thermal diffusivity a , and density ρ were measured independently from each other as temperature-dependent parameters within a temperature range spanning from 300 K to 773 K. Equation 2.1 shows the relationship between these properties [6, 9]:

$$\lambda(T) = c_p(T) \cdot a(T) \cdot \rho(T) \quad (2.1)$$

Density measurements were conducted at room temperature (RT) using Archimedes' principle. These measurements were carried out in both air and ethanol using a high-precision laboratory balance CPA 225D by Sartorius AG. To establish density for all three samples, five measurements of each alloy were performed to determine the average and estimate the mean deviation from the mean value. The temperature dependence of the density was assessed in conjunction with the coefficient of thermal expansion (α_{th}) using a vertical dilatometer with an Al₂O₃ differential measurement system (type L75 Platinum Series) by Linseis Messgeraete GmbH. Round samples, each with a diameter of 4 mm and a length of 20 mm, were employed for dilatometry. Reference parameters included the room temperature and the length of the sample at room temperature. For each material and temperature, three independent measurements on three separate specimens were conducted, with subsequent calculations of the average and standard deviation.

Thermal diffusivity measurements were performed using the laser-flash principle with a Linseis Messgeraete GmbH LFA 1250 laser-flash analyzer according to ASTM E1461 [125]. The samples, featuring a diameter of 10 mm and a thickness (L) of 2 mm, were ground using 1000 mesh SiC paper and coated with a thin graphite layer to enhance laser radiation absorption, ensuring precise measurements. Throughout the laser irradiation, an infrared sensor continuously monitored the temperature of the sample's upper surface. From the duration ($t_{1/2}$), required for the upper side of the specimen to reach 50% of its maximum temperature, the thermal diffusivity was estimated using Equation 2.2 [46]:

$$a = 1.38 \cdot \frac{L^2}{\pi^2 \cdot t_{1/2}} \quad (2.2)$$

A minimum of three independent measurements on three separate specimens were carried out for each material and temperature to determine the average a -value.

The specific isobar heat capacity c_p was determined using a Linseis Messgeraete GmbH HDSC PT-1600 differential scanning calorimeter (DSC) according to ASTM E1269 [126]. The procedure involved stabilizing the calorimeter, followed by the measurement of two empty crucibles to establish baseline corrections. Subsequently, calibration was performed using a sapphire specimen in one crucible. To ensure efficient heat transfer between the specimens and crucibles, the samples with a diameter of 4 mm and a thickness of 0.5 mm were ground with a 1000-mesh SiC paper. The prepared samples replaced the sapphire after calibration. The heating process remained consistent throughout baseline, calibration, and sample measurements, comprising a linear heating rate of 20 K/min from 300 K up to 773 K, a 1-minute dwell time, and subsequent cooling to RT. For each material under investigation, three independent test series consisting of three measurements each were conducted.

Finally, the thermal conductivity was determined using Equation 2.1 in combination with the specific heat capacity c_p , thermal diffusivity a , and density ρ . The corresponding standard deviation was computed following the Gaussian rule of error propagation.

2.2.4. Electrical resistivity

To measure the electric resistivity and the Seebeck coefficient, the four-wire measuring method with an LSR-3 system from Linseis Messgeraete GmbH was employed. Cylindrical samples, 4 mm in diameter and 10 mm in length, were utilized for these tests. A thermal gradient of 50 K was applied using a secondary heating source located at the bottom of the sample. A probe current of 100 mA was introduced. Three independent measurements on three distinct specimens for each material and temperature were carried out. The average values and standard deviations were subsequently calculated. By measuring the electrical resistance, a more detailed insight into the thermophysical properties can be achieved. This arises from the transport mechanisms of heat conduction in metallic materials. Following, the thermal conductivity in metallic ma-

materials is composed of several components, including a phononic contribution ($\lambda_{phononic}$) arising from lattice vibrations, an electronic ($\lambda_{electronic}$) and a magnonic contribution ($\lambda_{magnonic}$) resulting from electronic heat transfer [7–9]. As described in Ref. [8], the magnonic contribution is negligible and the thermal conductivity λ can be calculated using:

$$\lambda_{resulting} = \lambda_{electronic} + \lambda_{phononic} \quad (2.3)$$

Accordingly, the electronic contribution can be calculated using the Wiedemann-Franz-Lorenz law [6, 127]:

$$\lambda_{electronic} = T \cdot \sigma (L_0 - S^2) \quad (2.4)$$

In the above equation, S represents the Seebeck coefficient, σ stands for the electrical conductivity, which is the reciprocal value of the electrical resistivity, and L_0 is the Lorenz number. As the thermal conductivity ($\lambda_{resulting}$) and electronic contribution ($\lambda_{electronic}$) can be determined using Equations 2.1 and 2.4, respectively, the phononic contribution ($\lambda_{phononic}$) can be deduced from Equation 2.3.

2.2.5. Electron spin resonance

The experimental investigation of the electronic structure employed electron spin resonance (ESR). This technique provides crucial insights into electron properties in paramagnetic alloys, specifically revealing the existence of different electron subsystems and the impact of solutes on the electron state density at the Fermi surface ($D(E_F)$). In particular, the high sensitivity of the gyromagnetic factor (g -factor) to the inhomogeneity of the electron system forms the basis of this method. The g -factor describes the quotient of the measured magnetic moment and the predicted moment, therefore giving information about the electronic spins. Through the magnetic susceptibility, ESR enables the exploration of interactions between free and localized electrons, yielding quantitative data on isolated localized d-electrons (single substitutional d solute atoms) and superparamagnetic clusters (clusters of d atoms).

ESR measurements were carried out at 300 K. An Electron Paramagnetic Resonance (EPR) spectrometer Radiopan X-2244 was employed with a frequency (ν) of 9.3 GHz, microwave field power (P_{mw}) of ≈ 2 mW, the modulating field with modulation amplitude (H_m) of 3×10^{-1} mT, and modulation frequency (f) of 100 kHz. The sample thickness of 20 μm ensured negligible skin effect at temperatures exceeding 100 K. Measurements were conducted using two set-up geometries, i.e., with an external magnetic field (H_0) in the sample plane ($\Theta = 0^\circ$) and with H_0 orthogonal to the sample plane ($\Theta = 90^\circ$). This approach facilitated the exploration of g -factor anisotropy, a sensitive tool for identifying phase transitions. The CESR signal was recorded as a derivative of absorbed microwave power on the external magnetic field, with MgO: Cr³⁺ ($g = 1.9799$, number of spins $N = 3 \times 10^{14}$) serving as the reference. To avoid artifacts during the CESR signal registration, the absorption signal of the microwave power from the empty resonator was recorded before each measurement. The theoretical evaluation of this technique can be found in Refs. [38] and [39].

2.3. Results and discussion

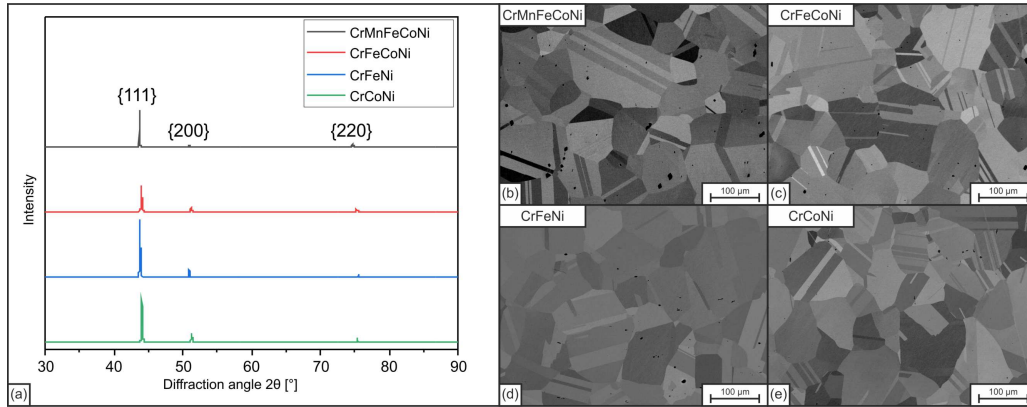
2.3.1. Composition and microstructure

Before considering the thermophysical properties of the investigated materials, one has to consider their microstructure and chemical composition to exclude or quantify unintended influences. The chemical composition of the four investigated high-entropy alloys is found to be close to the targeted equiatomic composition (Tab. 1). Moreover, the impurity concentrations (e.g., O and N) are relatively low (e.g., < 0.2 at.% O and < 0.004 at.% N). This lies within good agreement with the measured values in one of the previous studies, where the chemical composition has been investigated by X-ray fluorescence analysis and a similar manufacturing method was applied [70, 128], indicating that our processing route is reproducible. More importantly, any significant influence of O and N on thermophysical properties is not expected, owing to their relatively low concentrations. Representative XRD patterns in Fig. 2.1 suggest that the four alloys are single-phase fcc, which can be validated based on the position of the diffraction peaks and their microstructure shown in the BSE images. Due to the lattice-preferred direction, the $\{111\}$ signal exhibits a higher intensity than the $\{200\}$ and $\{220\}$ signals, which might be an artefact from swaging [121, 129].

Table 2.1.: Chemical compositions and O and N contents measured by EDS and carrier hot gas extraction of the investigated alloys in at.%.

Alloy	Cr	Mn	Fe	Co	Ni	O	N
CrMnFeCoNi	20.7 $\pm$ 0.3	20.2 $\pm$ 0.3	19.8 $\pm$ 0.5	19.7 $\pm$ 0.1	19.6 $\pm$ 0.4	0.138 $\pm$ 0.003	0.0020 $\pm$ 0.0002
CrFeCoNi	25.4 $\pm$ 0.3	-	16.3 $\pm$ 0.3	24.2 $\pm$ 0.5	24.1 $\pm$ 0.4	0.132 $\pm$ 0.002	0.0040 $\pm$ 0.0001
CrFeNi	33.6 $\pm$ 0.4	-	34.2 $\pm$ 0.2	-	32.1 $\pm$ 0.3	0.169 $\pm$ 0.008	0.0020 $\pm$ 0.0002
CrCoNi	34.1 $\pm$ 0.5	-	-	33.0 $\pm$ 0.5	32.7 $\pm$ 0.3	0.156 $\pm$ 0.005	0.0020 $\pm$ 0.0002

Corresponding lattice parameters obtained from the XRD patterns are shown in Tab. 2.2, with the experimental error being at most ± 0.1 %. Due to the manufacturing method and heat treatment, no significant segregation of the elements is expected, as shown in Ref. [70].

**Figure 2.1.:** a) XRD patterns and b)-e) BSE-images of the investigated high- and medium entropy alloys.

Since grain boundaries act as scattering sites for both phonons and electrons [20, 21], grain size measurements were conducted as described in section 2.2.2. The results are given in Tab. 2.2. On such a large scale, the effect of grain boundaries on the thermophysical properties, however, can be neglected [22, 130].

Table 2.2.: Lattice parameter $a_{lattice}$ in nm and grain size d in μm .

Alloy	$a_{lattice}$	d
CrMnFeCoNi	0.358	44 ± 1
CrFeCoNi	0.359	49 ± 5
CrFeNi	0.359	73 ± 7
CrCoNi	0.358	63 ± 10

2.3.2. Thermal conductivity

In the following sections, we present the temperature dependence of the factors contributing to the thermal conductivity (Eq. 2.1), namely density, specific heat capacity and thermal diffusivity. The temperature dependent properties are given in Fig. 2.2.

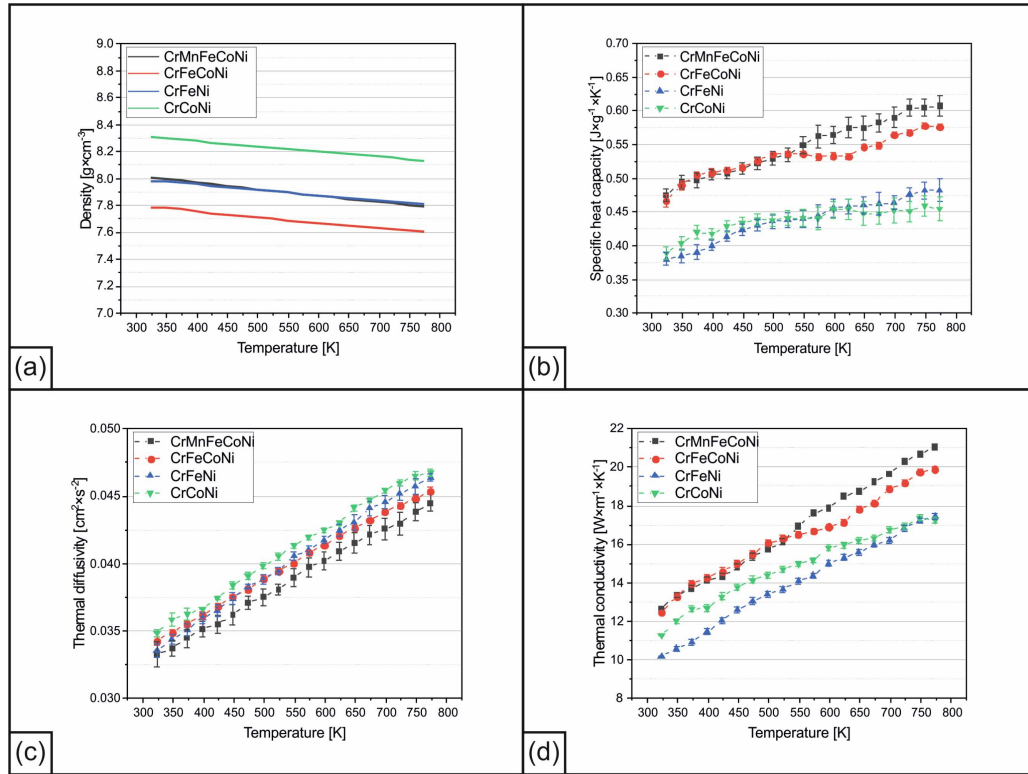


Figure 2.2.: a) Density, b) specific heat capacity, c) thermal diffusivity and d) resulting thermal conductivity of the investigated high- and medium entropy alloys between 300 and 773 K.

Density

The temperature dependent density of the investigated alloys is displayed in Fig. 2.2a. As the density is a parameter dependent on both weight and length, it is determined

by the corresponding elements and their (atom-) weight as well as the lattice parameter. The lattice parameters are shown in Tab. 2.2 and show similar values for all the investigated alloys, which fit well with the lattice parameters from previous studies [121, 131]. Additionally, these values strongly correlate with presented lattice parameters by *J. Coreño Alonso and O. Coreño Alonso* [132], who derived lattice parameters of various HEA and MEA by volume size factors and Vegard's law [133]. Since the lattice parameters of the four alloys do not differ by more than 1 % (Tab. 2.2, the differences in density at RT can be attributed to variations in the atomic weights of the constituent elements. For instance, as the atomic weights of the elements are 51.996 (Cr), 54.938 (Mn), 55.845 (Fe), 58.933 (Co), and 58.693 (Ni) [134], large Ni and Co contents result in denser alloys. For this reason, CrCoNi has the highest density. CrFeNi and CrMnFeCoNi exhibit a similar density because Mn and Co have low and high atomic weights, respectively, thereby canceling each other out.

When considering the temperature dependence of density, only minor differences are observed. This is a result of similar coefficients of thermal expansion (CTE, exemplary shown in Tab. 2.3). Comparable values were also reported in the literature [70, 77, 121].

Table 2.3.: CTE of the investigated alloys in $10^{-6}/\text{K}$, with the experimental error being at most $\pm 1\%$.

Alloy	373 K	473 K	573 K	673 K	773 K
CrMnFeCoNi	16.3	18.8	19.4	19.5	19.6
CrFeCoNi	15.63	18.0	18.7	18.8	18.8
CrFeNi	17.1	19.7	20.4	20.5	20.6
CrCoNi	15.2	17.5	18.1	18.2	18.3

Specific heat capacity

The measured specific heat capacity of the investigated alloys is found to increase with temperature. The slopes of the $c_p(T)$ -curves are similar for $T < 550\text{ K}$ in the four alloys, but CrFeCoNi exhibits a reduced slope at higher temperatures (see Fig. 2.2 b), indicating an exothermic reaction. However, as no sharp peaks are observed in Fig. 2b and the subsequent XRD pattern after DSC measurements show no influence of the measurement temperatures, this suggests that no phase transformation, neither magnetic nor structural, takes place in the investigated temperature range [77, 119,

135]. This correlates well with the previous results reported in the literature, where the Curie temperatures (T_C) for the alloys shown here are below 300 K, whereby the exact value is closely correlated to the Cr content of the alloys [77, 119, 135]. Nevertheless, it can be stated that increased chemical complexity leads to a higher specific heat capacity. This goes hand in hand with the analysis regarding thermal conductivity made by *Jin et al.* [77]. According to first-principle calculations, the specific heat capacity, which consists of magnetic, lattice, and electronic contributions, depends mostly on the latter two, with negligible electronic contributions [77]. Within a higher temperature range close to T_C , the magnetic part becomes more pronounced. Since the CrFeCoNi alloy shows a reduced c_p at temperatures above 500K compared to CrMnFeCoNi, this difference may be either attributed to magnetic and/or lattice contributions.

Since c_p of CrFeCoNi shows a decrease, an exothermic reaction is expected. Due to the water quenching, a metastable state might occur, which have been gradually shifted to a steady state. Following, with decreasing disorder the energy of the system has been lowered, resulting in a decrease of c_p . Based on DFT simulations, *Jin et al.* [77] suggested that SRO could form at low temperatures, thereby lowering the c_p value and the energy of the system if the atomic mobilities are sufficiently large. In a comparable system from *Sun et al.* [136], a slight decrease in c_p over a similar temperature range was observed that was attributed to SRO formation during the measurement. Additional and more recent investigations by *Andreoli et al.* [78] have shown the formation of SRO and confirmed their formation by first-principle simulations of the electronic density of states. Additionally, like already mentioned, significant influences might come from magnetic contributions to the specific heat capacity. A recent study from *Woodgate et al.* [137], showed that the magnetic configuration significantly influences SRO effects and can therefore be a determining factor regarding the CrFeCoNi signal. Since this could only be measured in CrFeCoNi, this could be the reason for the difference to the other alloys [137]. By employing ESR measurements, a more detailed insight on the electronic contribution to the specific heat capacity will be provided in section 2.3.3.

Thermal diffusivity

In former studies, we have shown for Fe-based alloys that thermal diffusivity plays a pivotal role in determining thermal conductivity [19, 23, 138, 139]. Thermal diffusivity is of immense importance when it comes to the time-temperature characteristics of

materials. This is emphasized in the basic principles of the heat conduction equation, underscoring its significant impact on the dynamic heat transfer [45]. Furthermore, the thermal diffusivity is determined by factors that influence both electronic and thermal heat transfer with the corresponding scattering of electrons and phonons, making this parameter highly important. For the alloys investigated in this study, the temperature dependent thermal diffusivity obtained by laser flash analysis is shown in Fig. 2.2c. Here, it is noteworthy that there are only minor differences in RT- and HT-thermal diffusivities. Despite the apparent similarity in these materials, a significant temperature dependency is noticeable. Nevertheless, when it comes to RT thermal diffusivity, CrCoNi shows the fastest heat transfer, followed by CrFeCoNi and CrFeNi, which show nearly identical thermal diffusivities at RT, while CrMnFeCoNi exhibits the slowest heat transfer between 300 K and 773 K. Interestingly, the three-element alloys (CrCoNi and CrFeNi) show a higher thermal conductivity than the quaternary and quinary alloys. This result can be attributed to the fact that alloying elements act as scattering sites for the phononic heat transfer, thus reducing thermal diffusivity and conductivity [140, 141]. In other words, for equatomic alloys, the higher the number of elements, the lower the thermal diffusivity.

A similar increase in thermal diffusivity with rising temperature is observed for all alloys studied. This increase suggests that the electronic contribution to the thermal diffusivity, which typically increases with rising temperature in metals and alloys with an fcc lattice, determines the temperature dependency, since it counteracts the increased phononic scattering occurring with rising temperature [141]. Compared to austenitic stainless steels (e.g., AISI 316L [138, 139]), the slopes of the $a(T)$ -curves in Fig. 2.2c are significantly larger for the HEA and MEAs. This difference may be attributed to the fact that some of the solutes in AISI 316L (e.g., C and Mo) have atomic radii that differ more strongly from that of the "average" matrix than in the HEA and MEAs. This results in more potent scattering sites for phononic heat transfer and thus a lower slope of the $a(T)$ -curve.

Thermal conductivity

According to Equation 2.1, the thermal conductivity is a result of multiplying the thermal diffusivity, specific heat capacity and density, which are all temperature dependent properties and accordingly show different temperature dependencies. When it comes to conventional alloys with fcc lattice, a significant effect of the thermal diffusivity on

the thermal conductivity can be noticed [23, 139]. Nevertheless, within the investigated equiatomic alloys, a minor impact of the thermal diffusivity is recognized (Fig. 2.2d). The most important influence is the specific heat capacity (Fig. 2.2b), which varies considerably between the HEA and MEAs. The alloys can therefore be classified in two groups, namely the MEAs consisting of three alloys CrFeNi and CrCoNi and the more complex MEA/HEA CrFeCoNi and CrMnFeCoNi, with CrFeNi and CrCoNi showing a lower specific heat capacity in comparison with the more complex alloys CrFeCoNi and CrMnFeCoNi. While the CrMnFeCoNi and the CrFeCoNi exhibit nearly identical $\lambda(T)$ -curves below 550 K (Fig. 2.2d), a similarity to the austenitic stainless steel AISI 316L at RT can be found, exhibiting a comparable thermal conductivity [138].

Electrical resistivity and resulting electronic thermal conductivity

As previously mentioned, the electronic state and its temperature dependent behavior plays a key role regarding the thermophysical properties of metallic materials. Therefore, the resistivity can be used to calculate the electronic contribution to the thermal conductivity. Both the electrical resistivity and electronic thermal conductivity are displayed in Figs. 2.3a and b, respectively. Additionally, the phononic contribution to the thermal conductivity as well as the electronic fraction are displayed in Figs. 2.3c and d. Note that the electrical conductivity is the reciprocal value of the electrical resistivity.

The electrical resistivity at RT of the four alloys strongly differs (Fig. 2.3a). The Cantor alloy CrMnFeCoNi shows the lowest resistivity and therefore highest electrical conductivity, followed by CrFeCoNi, CrFeNi, and CrCoNi. Since all of the investigated alloys have substantial Cr contents, the electrical resistivity is quite high, as Cr is known to reduce the concentration of free electrons in the spin-up conduction channel, decreasing the ability to conduct current [82]. In comparison to *Jin et al.* [119], the reported resistivity of the alloys CrCoNi, CrFeCoNi, and CrMnFeCoNi was lower at 300 K than the findings of this study. This difference could be attributed to variations in the manufacturing process, as *Jin et al.* [119] investigated CrCoNi and CrFeCoNi as single crystals, while CrMnFeCoNi had much larger grains than those alloys presented in our study. Consequently, direct comparisons between the two studies should be avoided.

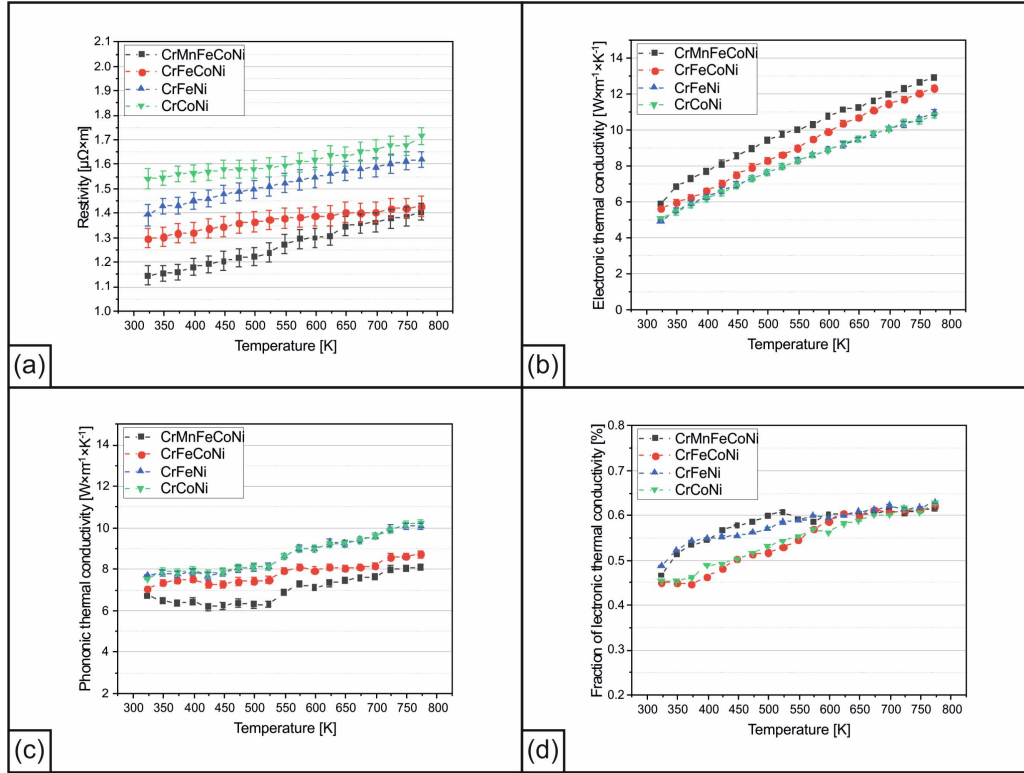


Figure 2.3.: a) Electrical resistivity, b) electronic and c) phononic thermal conductivity and fraction of the electronic thermal conductivity of the investigated high- and medium entropy alloys.

Regarding the temperature dependency of the alloys, CrFeCoNi shows a less pronounced temperature-dependent increase in resistivity. This correlation, which might be a result from SRO as discussed on the basis of the DSC measurements, has also been observed by *Andreoli et al.* [78], who were able to detect anomalies in the logarithmic derivate of resistivity that were a result from the high temperature formation of SRO. Nevertheless, CrFeCoNi shows a less pronounced temperature dependent increase in resistivity. In fcc metals and alloys, two relevant factors influence the electrical conductivity – electron scattering and electron excitation. In the latter case, an increase in electronic thermal conductivity with rising temperature, can be observed. This is due to the residual resistivity at 0 K, which is fairly high in these alloys, resulting in an almost linear increase in electronic thermal conductivity [119]. The resulting positive and nearly linear slope of the resistivity is affected by electron-phonon interaction and occurs due to the measurement temperatures that are higher than the Debye temperature [11]. In comparison to pure metals, where the phononic part is mostly negligible, these results show that the scattering of electrons is significant in the HEA and MEAs investigated here [12]. Therefore, the increase of electronic thermal conductivity leads to a positive slope of the overall thermal conductivity, which strongly correlates with T_C . Above T_C , an increase in thermal conductivity is expected [142]. This positive

temperature dependent slope comes from the fcc lattice and is determined by the thermal diffusivity, which is highly influenced by the electronic contribution. By comparing the electronic and phononic contributions with the overall trend in thermal conductivity, one can identify the electronic contribution as the main factor in the differing behavior. In the alloys CrMnFeCoNi and CrFeCoNi, the phononic contribution becomes less present. In contrast, the alloys CrFeNi and CrCoNi show higher phononic contributions, which is due to less scattering sites resulting from decreased complexity, so called mass disorder scattering [143], which gets even more relevant for higher temperatures. This decreased phononic thermal conductivity can be correlated with the DSC measurements, in which a higher complexity of the alloys leads to an increased specific heat capacity (Fig. 2.2b). As the complexity increases, phononic scattering and energy required to change the internal energy of the alloy increases, leading to a more pronounced harmonic contribution of c_p and corresponding lower phononic thermal conductivity.

2.3.3. Electron spin resonance

To get a closer insight into the electronic properties on an atomic scale, ESR measurements were carried out. Firstly, ESR allows to probe the electronic density of states (DOS), which provides crucial information about the distribution of electrons within the orbitals of a material. This information is fundamental for understanding the electronic structure and behavior of materials, which in turn influences their thermophysical and mechanical properties. In addition, ESR is sensitive to the presence of SRO in alloys [81]. SRO can have significant impacts on the material properties, including thermal conductivity and diffusivity, as already reported in the literature [77, 144–146] and seen in this study, especially regarding the differences in specific heat capacity in CrFeCoNi in comparison to the other HEA/MEA. Therefore, an in-depth understanding of SRO is crucial in tuning the properties of these group of alloys. One can detect and characterize SRO effects by measuring ESR signals, providing insights into the microstructural features that influence thermophysical behavior.

Therefore, ESR spectra of CrMnFeCoNi, CrFeCoNi and CrFeNi are shown in Fig. 2.4. Within the measurements, a weak but present CESR signal was only detectable in CrCoNi, showing the presence of effects that mask the signal of conduction electrons in all alloys, already giving a hint about SRO-effects in the investigated

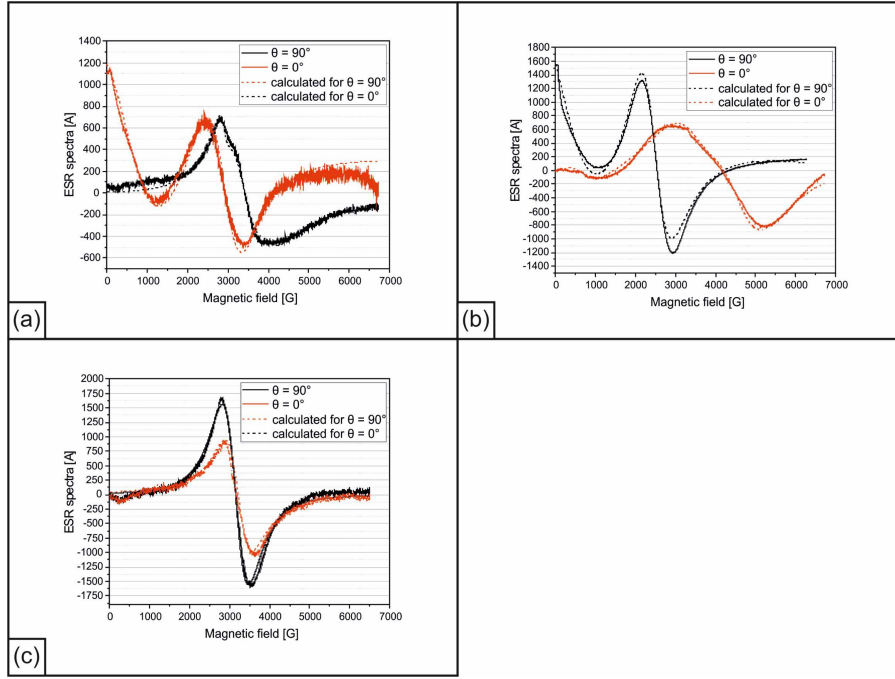


Figure 2.4.: ESR spectra of a) CrMnFeCoNi, b) CrFeCoNi, c) CrFeNi and measured in a sample plane of $\theta = 0^\circ$ and $\theta = 90^\circ$ relative to the magnetic field at RT.

HEA and MEAs. Since CESR was only detectable in CrCoNi the corresponding ESR spectra with the calculated CESR signals in $\theta = 0^\circ$ and $\theta = 90^\circ$ is displayed in Fig. 2.5.

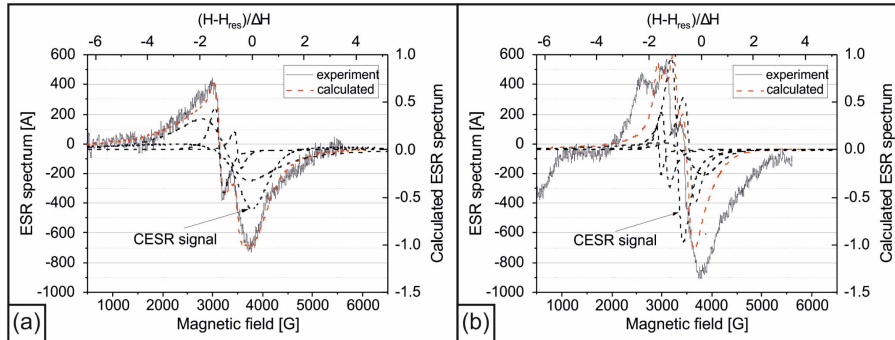


Figure 2.5.: ESR spectra of CrCoNi measured in a sample plane of a) $\theta = 0^\circ$ and b) $\theta = 90^\circ$ relative to the magnetic field at RT.

The observations regarding conduction electrons are due to paramagnetic and ferromagnetic absorption weakening the conduction electron signal. Therefore, no CESR was detectable in CrMnFeCoNi, CrFeCoNi and CrFeNi and only a weak CESR was detectable in CrCoNi. Regarding this, SRO is expected in all of the investigated alloys, since a CESR signal has to be present but could not be measured. The details of this

Table 2.4.: Resonance fields, g-values and amplitudes of the ESR-spectra of the investigated alloys with H in the sample plane ($\theta = 0^\circ$)

Alloy	H_{res} in G	$g - value$	δH in G	Amplitude in A
CrMnFeCoNi	$H_{FMR}=500$	-	1500	120
	2900	2.317	800	110
CrFeCoNi	$H_{FMR}=200$	-	1500	2212
	2500	2.689	350	2528
CrFeNi	3150	2.135	560	89
CrCoNi	3136	2.144	157	18
	3267	2.058	835	11
	3501	1.920	130	14
	CESR: 3788.6	1.770	522	26

Table 2.5.: Resonance fields, g-values and amplitudes of the ESR-spectra of the investigated alloys with H in the sample plane ($\theta = 90^\circ$)

Alloy	H_{res} in G	$g - value$	δH in G	Amplitude in A
CrMnFeCoNi	$H_{FMR}=-$	-	-	-
	2900	2.3198	200	20
	3400	1.980	500	90
CrFeCoNi	$H_{FMR}=750$	-	800	252
	3450	1.920	1200	885
	4580	1.477	1200	1664
CrFeNi	3112	2.162	1800	6
	3220	2.0895	500	55
CrCoNi	2595.8	2.5916	127	11
	2807	2.3964	237	16
	3187	2.1106	338	42
	3584.5	1.880	338	24
	CESR: 3964.8	1.700	1523	32

phenomenon will be described in the following. As the magnetic field aligns with the sample plane, ESR-resonance fields exist in all samples, as shown in Tabs. 2.4 and 2.5.

While the signals exhibit similarities, the resonance field shifts in the presence of ferromagnetic inclusions. Consequently, the signal at $H_{res}=3150$ G is attributed to the paramagnetic center (PC) with a g -factor of 2.135. PC are inherent in solid solutions of transition metals due to charge compensation or imperfections in the crystalline structure, for example, stacking faults. By substituting Fe with Ni or Cr, a change in the free electron system occurs, making these atoms paramagnetic. As reported, the correlation of g -value and magnetic susceptibility of different electronic systems can be used to identify different atomic distributions [39]. Firstly, magnetic susceptibility is influenced by free electrons, including itinerant electrons, d1-subsystems of d-electrons

in combination with isolated atoms and d2-subsystems or superparamagnetic clusters (clusters of d-atoms).

Therefore, the existence of paramagnetic influences is suggested by the presence of $g_{\parallel}=2.135$, $g_{\perp}=2.34$, pointing out the presence of Ni^{2+} [147]. This can be seen in the ESR spectrum of CrFeNi at $\theta = 90^\circ$. This signal represents an averaged powder spectrum as Ni^{2+} is randomly distributed. The second paramagnetic signal, characterized by a g -factor of 1.98, corresponds to the PC Cr^{2+} with an anisotropic $g_{\theta=0^\circ}=1.98$ and $g_{\theta=90^\circ}=1.95$. The broad width of these signals impedes their observation at $\theta = 0^\circ$. Accordingly, there is a direct connection between the ESR signal of CrFeNi as described here and SRO in this particular alloy.

The ferromagnetic signal observed at low fields arises from the presence of ferromagnetic clusters. To ensure that the resonance field is shifted to these lower fields by the anisotropic field and demagnetization field, these fields must be sufficiently large, such that the ferromagnetic atomic scale areas are primarily composed of Fe. By employing the theory of angular dependence of ferromagnetic resonance field [148] and considering the anisotropy field A much larger than the demagnetization field, expressed as $B_2 = 2\pi M(n_2 - n_3)$ and $B_3 = 2\pi M(n_1 - n_3)$, with M being the magnetization of the ferromagnetic particle, and n_1, n_2, n_3 are the coefficients of the shape anisotropy, one can derive:

$$H_{res,\theta=0^\circ} = 2B_3 - B_2 + ((\omega_{mw}/\gamma_L)^2 + B_2^2)^{0.5} \quad (2.5)$$

$$H_{res,\theta=90^\circ} = B_3 - 2B_2 + ((\omega_{mw}/\gamma_L)^2 + B_3^2)^{0.5} \quad (2.6)$$

Given $(\omega_{mw}/\gamma_L) = 3400 \text{ G}$, $H_{res,\theta=0^\circ} = 200 \text{ G}$, and $H_{res,\theta=90^\circ} = 750 \text{ G}$, solving the equation yields $B_3 = -1241 \text{ G}$ and $B_2 = 819.2 \text{ G}$. These results collectively indicate that the crystalline structure contains a significant number of grains, with grain boundaries harboring numerous PC. Therefore, a SRO can be attributed in all investigated alloys. Since it was possible to obtain CESR signals in CrCoNi, a comparison of the g -factor with literature values will be carried out. By this, the concentration of free electrons cannot be quantified but estimated in a qualitative manner. The g -value of the 1.7 of CrCoNi in the CESR spectra is lower than that found in austenitic stainless steels from other studies [38, 80]. The CESR signal shape and low g -value indicate a strong exchange interaction of free electrons with PC [149] and s-d hybridization, which

decreases DOS at the Fermi surface. Due to this decreased concentration, a higher electrical resistivity and therefore lower electronic thermal conductivity of CrCoNi is expected, which is validated by the thermophysical properties (see Fig. 2.3), similar to previous observations in austenitic stainless steels reported in literature [130, 145, 146].

By taking the DSC measurements of c_p in CrFeCoNi (Fig. 2.2b) and the SRO shown by ESR measurements into account, one has to consider the formation of SRO in CrFeCoNi during the heating stage of the DSC measurement. Additionally, *Andreoli et al.* [78] showed a SRO formation in this alloy after subsequent heating cycles. Therefore, a decelerated formation of SRO is expected in comparison to the other alloys, since a weak exothermic signal could be detected by DSC, showing a non-equilibrium state after homogenization in CrFeCoNi. According to first-principle calculations by *Niu et al.* [150] in the CrFeCoNi alloy, ordering of Cr takes place to minimize the systems energy, giving this arrangement an energetic minimum, leading to a decrease in the specific heat capacity while heating. According to *Bykov et al.* [151] and *Jin et al.* [77], these effects result from K-state transitions due to heating that lead to SRO. As all other materials have shown SRO directly after annealing, we were not able to show a significant influence on the thermophysical properties in CrMnFeCoNi, CrFeNi and CrCoNi, in contrast to what has already been shown by simulations [78]. This might be a result from magnetic effects, as CrFeCoNi is the only alloy that shows a ferromagnetic resonance (FMR) in both alignments of the magnetic field. As shown by *Woodgate et al.* [137], the magnetism is a significant factor regarding SRO effects and therefore might influence the magnetic contribution to the specific heat capacity significantly. Additionally, the Cr-Cr combination, as shown by *Andreoli et al.* [78] and described as Cr^{2+} here, is a direct result of the orientation of magnetic moments.

2.4. Conclusion

This study presents an investigation of the temperature-dependent thermophysical properties of a high-entropy alloy and three medium-entropy alloys, i.e., CrMnFeCoNi, CrFeCoNi, CrFeNi, and CrCoNi, respectively. Measurements were conducted between RT and 773 K, using the dynamic measurement principle to access density, thermal expansion, thermal diffusivity, and specific heat capacity individually and temperature dependent. This procedure enabled a closer understanding of the influences on the overall thermal conductivity and its temperature dependent behavior of the in-

vestigated alloys. Additionally, the electrical resistivity was systematically measured, allowing for the application of the Franz-Wiedemann law. Subsequently, the Franz-Wiedemann law was utilized to compute the electronic contribution to the thermal conductivity. This approach provided a detailed understanding of independent parameters. By ESR-measurements, an insight into SRO effects in the investigated CCAs was done. Key findings regarding the thermophysical properties of the investigated HEA and MEAs are:

- In contrast to iron-based alloys, thermal diffusivity did not emerge as a significant factor in distinguishing the materials studied.
- The specific heat capacity predominantly influenced variations in the resulting thermal conductivity.
- With increasing chemical complexity, the specific heat capacity and the corresponding thermal conductivity increased.
- Phononic contribution to thermal conductivity increases with reducing chemical complexity, whereas higher complexity leads to an increased electronic contribution to thermal conductivity.
- Short-range ordering in the investigated alloys has a significant influence on the specific heat capacity of CrFeCoNi.

Further steps regarding the thermophysical properties of the HEA/MEA will include analyzing the thermophysical properties at low temperatures beginning at 77 K with corresponding ESR measurements to quantitatively assess the concentration of free electrons through the temperature dependency of the g -factor.

Chapter 3

Impact of Thermophysical Properties of High-Alloy Tool Steels on Their Performance in Re-Purposing Applications

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Abstract

Resource efficiency and circularity in the context of sustainability are rapidly gaining importance in the steel industry. One concept regarding circular economy is “repurposing”. In the context of this work, worn-out machine circular knives are used to produce new chisels for woodturning. The chisels can be extracted parallel or perpendicular to the rolling direction of the primary production process, resulting in an associated carbide orientation of the repurposed tool. The rolling direction, and therefore carbide alignment, will influence the wear resistance and the thermophysical properties, whereby the thermal conductivity will determine the temperatures at the tip of the chisel. Therefore, the thermal conductivity was investigated with the dynamic measurement method, where the specific heat capacity, density and thermal diffusivity of the extracted chisels and industrial reference chisels were measured separately. Moreover, the electrical resistivity was measured in order to calculate the electronic thermal conductivity according to the Wiedemann–Franz–Lorenz law. It was shown that all of these parameters exhibited different degrees of variability with rising temperature. In a detailed analysis, the thermal diffusivity could be identified as an essential parameter of thermal conductivity. By taking two conventional chisels with different chemical compositions and heat treatments into account, it can be seen that the microstructure determines the thermophysical properties. Considering the carbide direction, the chisels that were extracted parallel to the rolling direction showed differing thermophysical properties. Therefore, the carbide orientation is shown to play a significant role regarding the heat dissipation at the cutting edge, because differences, especially in the electronic thermal conductivity in the parallel and perpendicular extracted chisels, can be measured. In addition to the wear resistance factor, the thermal conductivity factor now also supports the removal of the repurposed chisels parallel to the rolling direction.

Keywords: thermophysical properties; thermal conductivity; thermal diffusivity; tool steels; electronic thermal conductivity; repurpose; circular economy

3.1. Introduction

Steel is a universally applicable material and therefore essential for today's economy and society; for instance, the raw steel production figures have doubled in the last 20 years [152]. With regard to sustainability, steel exhibits a high potential for resource efficiency because of its durability and a recyclability of nearly 100%. Nevertheless, the recycling of steels rarely achieves this efficiency due to contaminations even in remelting in basic oxygen or electric arc furnaces [153]. In addition, this type of recycling produces greenhouse gases, which must be considered as well.

According to *Potting et al.* [154], three different groups of the so-called 10 R-list can be identified in terms of the degree of circularity. The “Recycling” and “Recover” approaches are in the group with the lowest degree of circularity, whereas high degrees are preferable. The highest degrees of circularity can be achieved by the strategies “Refuse”, “Rethink” and “Reduce”. Classified in group two are the strategies “Re-use”, “Repair”, “Refurbish”, “Remanufacture” and “Repurpose”.

The strategy used here belongs to the “Repurpose” category, in which an old and no-longer-usable product is converted into another product with a different application [154]. This enables the use of raw materials within an extended life cycle, improving the carbon footprint massively. Different approaches have been studied in the literature regarding different industries; for example, the cement industry [155] or even the production of mineral wool [156]. In this work, the concept of “Repurpose” is applied to worn-out machine circular knives used in paper-cutting processes. Blanks for woodturning chisels were taken out of the circular knives and implemented in the conventional production process in order to maximize the material efficiency [157]. The manufacturing process of the machine circular knife determines the microstructure—or, more specifically, the carbide orientation—of the woodturning chisels. The chisels can be taken out along or across to the primary rolling direction [158]. As examined in previous works, the relative general orientation of these microstructural constituents influences critical macroscopical properties related to their system-related performance, such as abrasive wear resistance and maximum service temperature [23, 34, 159].

The service life of the extracted chisel depends mainly on the wear during woodworking. Wear describes the progressive loss of material from the surface of the base body in a tribological system, whereby the tribological system is determined by the base body in a relative motion to a counter body, sometimes in combination with an intermediate medium [160, 161]. Therefore, the wear resistance is not a material property,

but a property of a specific material in the given tribological system [160, 161]. When relative motions in a tribological system occur, heat results from the energy lost due to friction between the base and the counter body. Due to the high rotational speed and the high thrust in woodworking, high temperatures are therefore generated at the cutting edge, which as a result is a decisive factor for the material selection.

By combining these factors, the chisel underlies a coupled thermomechanical problem. Besides the wear resistance, the thermal conductivity is a further governing parameter which determines the temperature at the cutting edge. Higher conductivities are favourable because of an improved heat dissipation off the cutting edge. Furthermore, both parameters are strongly temperature-dependent and have to be taken into account when considering a tribological system, especially when a higher thermal conductivity lowers the operating temperature and thus results in a higher hardness and increased wear resistance during operation [159, 162]. The hardness and wear resistance is furthermore strongly dependent on the temperature, making this factor even more relevant [162, 163]. The thermal conductivity is determined by the chemical composition, as well as the heat treatment and the resulting microstructure [23, 34, 159, 164]. In particular, the carbide morphology and orientation, as well as the solution state of carbon in tool steels, plays a significant role in the thermal conductivity [23, 34, 159].

In the scope of this work, the thermophysical properties of the repurposed woodturning chisel made out of a lederburitic cold work tool steel will be described and evaluated by comparing them with those of a conventional chisel made of a carbon martensitic tool steel and a performance chisel made of a high-speed steel as benchmark materials. In particular, the repurposed chisel can be taken out across and along the rolling direction, a decision which might influence the thermal conductivity and thus has to be studied. In particular, the influence of the carbide morphology regarding the chisel extraction, as well as the influence of the tempering behavior of the investigated alloys on the thermophysical properties, is of special interest. Due to technological challenges in the sample extraction campaign, this work investigates the thermal conductivity by two independent routes: namely, using the dynamic indirect measurement method and the Wiedemann–Franz–Lorenz law to shed light onto its electronic component [42]. In all cases, the temperature dependency was considered.

3.2. Materials and Methods

3.2.1. Materials and Metallography

Repurposed woodturning chisel blanks were taken out of the worn-out machine circular knives parallel and perpendicular to the carbide direction by laser cutting; the analogue of the primary hot-rolling and its transversal direction. Fig. 3.1 a, b shows the selected axis system. Throughout this work, reference to the specimen or micrography orientation will be made using the following nomenclature: rolling direction (RD), transversal direction (TD), and normal direction (ND).

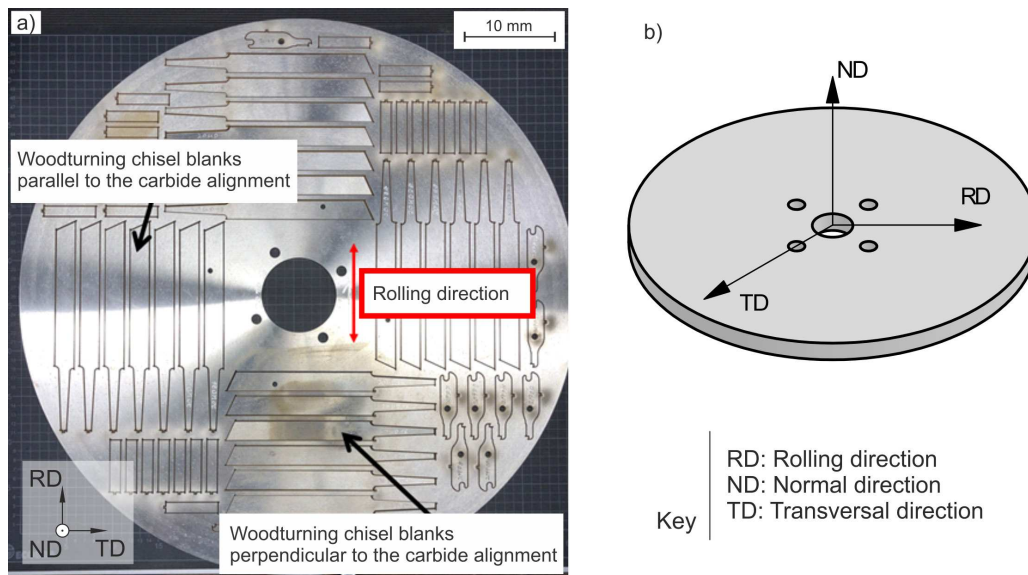


Figure 3.1.: (a) Worn-out machine circular knife with repurposed chisel blanks, taken out in the rolling and transversal directions (RD, TD, respectively). (b) Schematic diagram of the axes system selected.

The blanks were then manufactured into ready-to-use chisel shapes “A 20” according to DIN 5144 [165]. Benchmark chisels are also considered as a standard version according to this shape. The repurposed chisels were made of the cold work steel D2, and the benchmark chisels were made of the tool steel L2 and the high-speed steel M2, respectively. The corresponding chemical compositions are shown in Tab. 3.1. Optical emission spectrometry was carried out to determine the chemical composition with an emission spectrometer from OBLF GmbH, Witten, Germany. All materials were

Table 3.1.: Chemical composition of the investigated alloys in wt.%.

Alloy	C	Si	Mn	Cr	Mo	W	V	Fe
L2	0.78	0.23	0.58	0.29	–	–	0.12	Bal.
M2	0.79	0.33	0.34	3.84	4.66	6.28	1.82	Bal.
D2	1.52	0.35	0.43	11.44	0.68	–	0.73	Bal.

produced by casting, hot forming and a subsequent heat treatment, consisting of hardening and tempering according to industrial conditions (Tab. 3.2). For metallographic investigations, samples were cut from the three chisels. The samples were ground with SiC paper and were subsequently polished with a diamond suspension with a mean grain size of 6, 3 and 1 μm .

Microscopic images were obtained with a Vega 3 SHB SEM by TESCAN ORSAY HOLDING, a. s, Brno, Czech Republic, using secondary electron contrast with a voltage of 20 kV and a working distance of 10 mm.

Table 3.2.: Heat treatment of the investigated alloys

Alloy	L2	D2	M2
Hardening	85°C/6 min/ Oil	1055°C/30 min/ Chill hardening to 70°C	1210°C/15 min/ Furnace cooling
Tempering	200°C/70 min/ Salt water	3×530°C/480 min/ Furnace cooling	3×530°C/120 min/ Furnace cooling

3.2.2. Thermophysical Properties

Thermal Conductivity

The thermal conductivity λ was first determined by the dynamic indirect measurement method, whereby the separate and temperature-dependent parameters of specific heat capacity c_p , thermal diffusivity a and density ρ are measured in a temperature range of room temperature up to 500°C (Equation 3.1) [9, 42]:

$$\lambda(T) = \rho(T) \cdot a(T) \cdot c_p(T) \quad (3.1)$$

The specific isobar heat capacity c_p was determined using a differential scanning calorimeter type HDSC PT-1600 by Linseis Messgeraete GmbH, Selb, Germany. After stabilizing, two empty crucibles were measured for baseline correction. Calibration with a sapphire specimen in one crucible was performed immediately afterwards. Samples with a diameter of 4 mm and a thickness of 0.5 mm were ground by 1000 mesh SiC paper to ensure a good heat transfer between specimen and crucible. They replaced the sapphire after calibration. Heating remained unchanged between baseline, calibration and sample measurements. The program consisted of a linear heating rate of 20 K/min up to 500°C, a dwell time of 1 min and cooling to room temperature. Three independent test series were carried out for each investigated material.

The density was measured at room temperature using Archimedes' principle. Measurements were performed in air and ethanol, subsequently, using a high-precision laboratory balance CPA 225D by Sartorius AG. The room-temperature density of all three samples was determined in a series of five different measurements. Temperature dependency was determined by combination with the thermal expansion coefficient α_{th} , which were measured using a vertical dilatometer with an Al₂O₃ differential measurement system type L75 Platinum Series by Linseis Messgeraete GmbH, Selb, Germany. Round samples with a diameter of 4 mm and a length of 20 mm were investigated by means of dilatometry. Reference parameters were the room temperature as well as the length of the sample at room temperature. Three independent measurements on three separate specimens were carried out for each material and temperature. The average and the standard deviation were then calculated.

The thermal diffusivity was measured by the laser-flash principle using a laser-flash analyzer type LFA 1250 by Linseis Messgeraete GmbH, Selb, Germany. The samples with a diameter of 10 mm and a thickness L of 2 mm were ground with 1000 mesh SiC paper and coated with a thin graphite layer to maximize the absorption of the laser radiation to ensure a precise measurement. The sample upper surface temperature was constantly monitored during laser irradiation by an infrared sensor. Thermal diffusivity was determined by the $t_{1/2}$ time, which is the required time for the upper side of the specimen to reach 50% of its maximal temperature (Equation 3.2) [46]:

$$a = 1.38 \cdot \frac{L^2}{\pi^2 \cdot t_{1/2}} \quad (3.2)$$

At least three independent measurements on three separate specimens were executed for each material and temperature. The average thermal conductivity according to

Eq. 3.1 was calculated using their mean values. The standard deviation of the thermal conductivity was then calculated according to the Gaussian rule of error propagation. Unfortunately, the extraction of the laser-flash specimens was not possible in the rolling (RD) and transversal directions (TD) due to the required geometry being at odds with the knife thickness (the thickness was less than the required sample diameter of 4 mm, Figure 3.1). Instead, the laser-flash samples were cut out in the normal direction of the disks (ND) (Figure 3.1). Thus, a direct comparison of the thermal conductivity in the orientations of interest was not possible. The next subsection outlines the alternative approach that makes a quantitative evaluation possible.

Electrical Resistivity

Resistivity and Seebeck coefficient measurements were performed by the four-wire measuring method using an LSR-3 system by Linseis Messgeraete GmbH, Selb, Germany. Cylindrical samples with a diameter of 4 mm and a length of 10 mm were used. The thermal gradient of 50°C was applied by a secondary heating source on the bottom of the sample. The probe current was applied with a magnitude of 100 mA. Three independent measurements on three separate specimens were carried out for each material and temperature. The average and the standard deviation were then calculated. The thermal conductivity consists of different components, namely a phononic contribution by lattice vibrations, an electronic, and a magnonic contribution, these being independent of each other [7–9]. The magnonic contribution is particularly small and can be neglected in this case [8]. Thereby, a calculation of the resulting thermal conductivity was obtained according to Equation 3.3:

$$\lambda_{resulting} = \lambda_{electronic} + \lambda_{phononic} \quad (3.3)$$

The electronic contribution can be calculated using the Wiedemann–Franz–Lorenz law [42, 127]:

$$\lambda_{electronic} = T \cdot \sigma (L_0 - S^2) \quad (3.4)$$

where the S is the Seebeck coefficient, σ is the electrical conductivity, and L_0 is the known Lorenz number. The consideration of the electronic part enables the differentiation and influence of the parallel and perpendicular extraction of repurpose chisels on the thermal conductivity, because the samples are cut out in the transversal (TD) and rolling direction (RD), enabling a systematic view of the influence of the carbide morphology.

3.3. Results and Discussion

As already mentioned, the thermal conductivity of the investigated alloys differs due to their chemical composition and heat treatment (Fig. 3.1) [23, 34, 159]. Therefore, first analysis has to be performed regarding the microstructure of the investigated tool steels.

3.3.1. Microstructure of the Investigated Alloys

The investigated tool steels showed significant differences in their microstructure and resulting properties (Fig. 3.2). The low alloyed tool steel L2 showed no hard phases and a fully martensitic microstructure. Regarding the high-speed steel M2, hard phases of type M_2C , M_6C and MC were present in a fully martensitic matrix. The cold-work tool steel D2 is characterized by eutectic carbides of the type M_7C_3 , as shown by *Kronenberg et al.* [158]. As already mentioned, the larger eutectic carbides are aligned parallel to the primary rolling (RD) direction, which can be seen clearly in the SEM image [158].

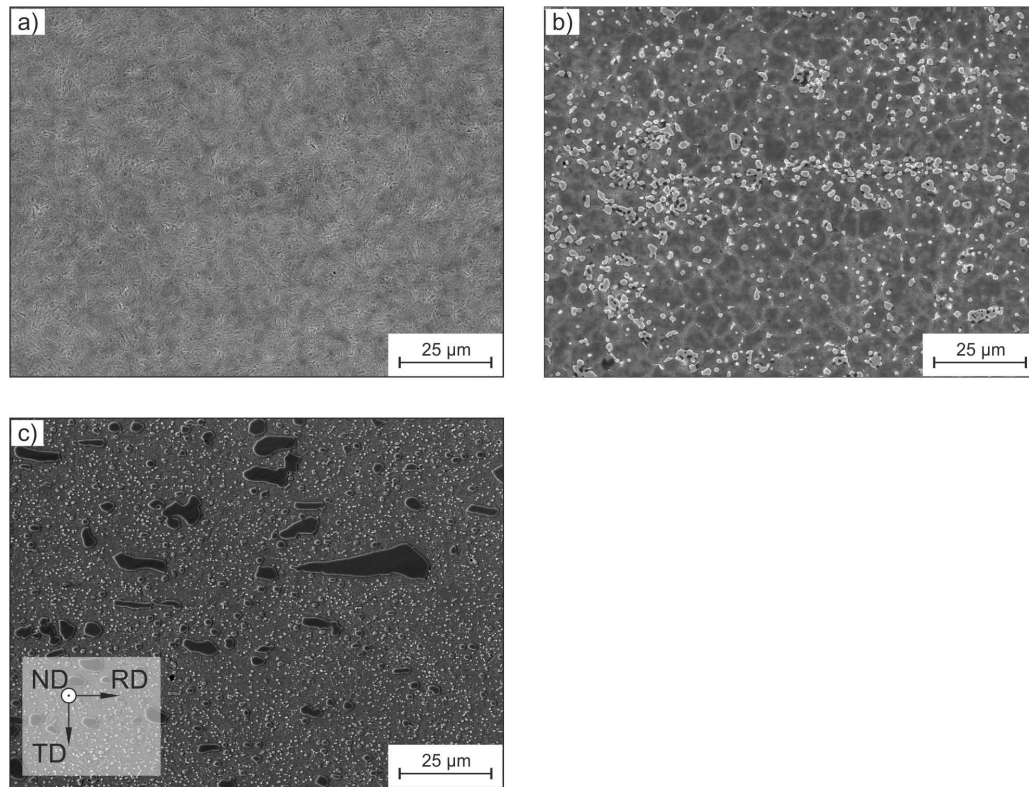


Figure 3.2.: SEM images of (a) tool steel L2, (b) high-speed steel M2 and (c) ledeburitic cold-work steel D2 in the orientation given in the provided axes.

3.3.2. Thermophysical Properties as a Function of Temperature

Thermal Conductivity

Fig. 3.3 a presents the thermal conductivity of the tool steels in a temperature range from room temperature up to 500°C. It is noteworthy that the measurement temperature was lower than the tempering temperature for the M2 and D2 alloy, while it exceeded the tempering temperature of the L2 alloy. As stated in the previous section, a differentiation between the thermal conductivity of the D2 alloy in the rolling (RD) and transversal directions (TD) was not possible using the dynamic measurement method. The material specific measurements show that the thermal conductivity of the tool steels differed in the whole temperature range. The alloy L2 had the highest conductivity at 60°C, which is approximately twice as high as the conductivity in the cold-work D2 and over 10 W/mK higher than in the high-speed steel M2. The temperature-dependent slope of the investigated materials show differences, especially

when comparing the L2 alloy to the cold-work and high-speed steel. It is well described in the literature that microstructural imperfections and impurities influence thermal conductivity [8, 23, 141]. These imperfections and impurities are a result of the chemical composition and heat treatment, resulting in a microstructure with carbides and a lattice with a high dislocation density due to the martensitic state. This microstructure assigns an increased number of scattering sources for lattice vibrations and electronic heat carriers, reducing the thermal conductivity, explaining the differences in the thermal conductivity.

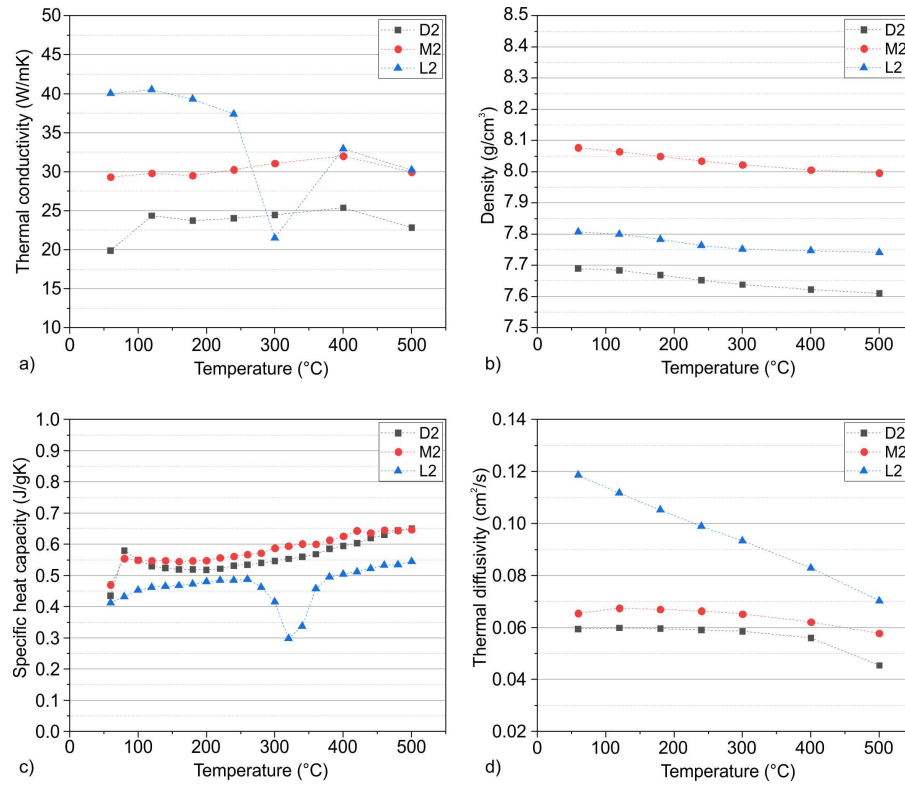


Figure 3.3.: Thermophysical properties of the investigated alloys according to the dynamic measurement method for the calculation of the (a) thermal conductivity using the (b) density, (c) specific heat capacity and (d) thermal diffusivity.

A more detailed analysis of the influences and resulting properties is therefore necessary and can be achieved with the help of the individual parameters of the thermal conductivity, namely the density, specific heat capacity and thermal diffusivity, and by consideration of the microstructure.

The temperature-dependent density of the four tool steels is displayed in Fig. 3.3 b. The alloy M2 showed the highest density due to the high contents of the heavy elements Mo and W. The tool steel L2 had a similar density to pure Fe through its low

concentrations of alloying elements. The Cr-alloyed steels showed a lower density due to the formation of M_7C_3 carbides, which have a lower density than pure Fe [23]. Only small differences of the temperature dependence of the alloys were detectable, due to their similar matrix microstructure.

Fig. 3.3 c shows the specific heat capacity as a function of the temperature. The trends present show an increase with rising temperature due to the excitement of lattice vibrations. The L2 tool steel was characterized by the lowest values across all studied materials; the specific heat capacity indicates the scattering of phonons in martensitic steels [34]. Through the absence of carbides (Fig. 3.2), the phonons are less scattered, which leads to a lower phonon scattering. Another effect is the increase in phononic scattering through alloying elements [26]. According to *Williams et al.* [26, 27], alloying elements are scattering sources as a result of mass differences and induced strain fields in the lattice. The lowest matrix alloy concentration in the tool steel L2 leads to less phononic scattering in the matrix, in addition to previously described effects. As a result, the system requires less energy to increase the temperature and internal energy, respectively. The drop at temperatures around 300°C is due to precipitation effects, which are a result of the single tempering stage at 200°C (Tab. 3.2). Because of the carbide precipitation, the hardness of the matrix decreases, disabling the deployment of the L2 tool steel in applications that exceed process temperatures of 300°C.

With respect to the two carbide-rich tool steels D2 and M2, a higher specific heat capacity can be detected. Due to the high content of nanometer sized tempering carbides in high-speed steels, which are finely dispersed in the matrix [166], the scattering of phonons increases and leads to a higher specific heat capacity. By comparison with the cold-work steel D2, the carbides were smaller and evenly distributed in the high-speed steel and coarser in the cold-work steel, giving the alloy D2 a lower specific heat capacity.

Thermal diffusivity is a central parameter of thermal conductivity and is defined as the time-dependent component. The thermal diffusivity is determined by factors that also influence the electrical resistivity and the specific heat capacity, because it reflects both electronic and phononic contributions and therefore scattering of those components. By contrasting Figure 3.3 a and d, it can be stated that the thermal diffusivity governs the overall trend of the thermal conductivity.

Considering the thermal diffusivity, the tool steel L2 with the single-phase martensitic matrix showed the fastest heat transfer. As already mentioned, carbides act as impurity sources, thus scattering phonons and reducing the thermal conductivity and diffusivity [23, 140, 141, 159]. Due to this relationship, the alloy L2 also featured the highest thermal conductivity and thermal diffusivity (Fig. 3.2 and Fig. 3.3 d). The decrease

in the thermal diffusivity results from increased phonon–phonon and phonon–electron scattering, hindering the heat transfer.

The M2 and D2 steels showed a significantly lower diffusivity at low temperatures due to increased scattering by carbides. In contrast to the alloy L2, the thermal diffusivity of the tool steels M2 and D2 was only slightly temperature-dependent. This result is due to the opposing influences of the decreasing effect of carbides and other scattering sources and enhancing influences of the matrix. It is well known that in high-alloyed matrices, the concentration of free electrons increases with temperature, enabling a higher thermal conductivity and diffusivity of the matrix [8, 23, 167]. It is also well reported in the literature that Cr reduces the concentration of free elements due to enhanced scattering of conduction electrons in the spin-up conduction channel [82]. Nevertheless, the tempering of martensitic steels will increase the thermal diffusivity of the matrix, which occurs especially at higher temperatures [23]. This effect results from the precipitation of tempering carbides, reducing the scattering due to less C and Cr in the matrix. At higher temperatures, the scattering effects dominate due to the interaction of thermally activated phonons and electrons, thus decreasing the diffusivity even more.

Electrical Conductivity and Electronic Thermal Conductivity

To overcome the limitations in the extraction of laser-flash specimens from the chisels, an approach was used based on the electrical conductivity and the Wiedemann–Franz–Lorenz law. Thanks to the more accommodating sample geometry of the specimens for the determination of the electrical resistivity and the Seebeck coefficient, it was possible to measure the influence of the carbide orientation on these properties. This effectively enables a quantitative analysis of the thermal conductivity by means of the electronic part of the thermal conductivity. It is worth mentioning that both the resistivity and the electronic thermal conductivity are proportional to the number of conduction electrons in a metal [8, 168].

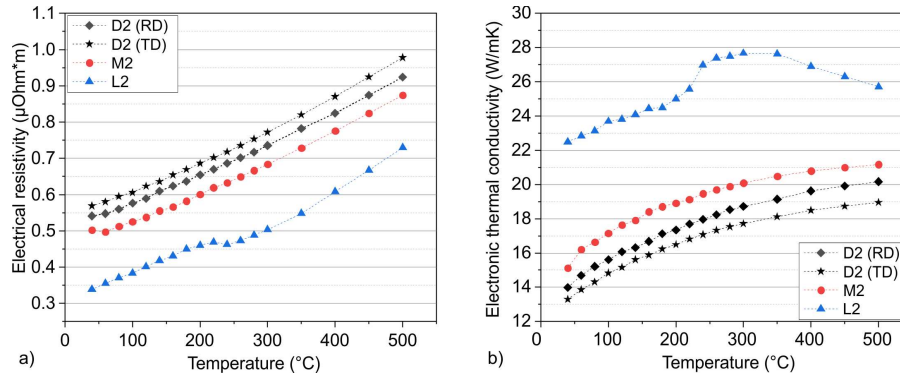


Figure 3.4.: Electrical properties as a function of temperature, regarding the (a) resistivity and (b) electronic thermal conductivity.

The electrical resistivity is displayed in Fig. 3.4 a. As with the thermal conductivity, the alloy L2 had the highest electrical conductivity, which is the reciprocal value of the electrical resistivity. The M2 and D2 tool steels showed a lower electric conductivity. This is due to the influence of Cr on the electronic conduction behavior that was already mentioned [82]. When considering the temperature dependence, it is noticeable that the electrical resistivity increases, which is in unison with Matthiessens' rule because of the scattering of electrons with the thermally activated phonons with rising temperature [168]. The temperature-dependent slope was similar for all alloys. Nevertheless, the L2 alloy showed a drop in the resistivity, which could be due to the precipitation of C, leading to a less strained martensite. Such a process is expected to decrease the electron–phonon scattering in the matrix, resulting from fewer defects in the lattice which are able to increase the electrical and thermal conductivity.

Of special interest is the influence of the carbide orientation of the D2 tool steel on electrical resistivity. It can be seen that the electronic thermal conductivity of the parallel extracted samples is higher than the conductivity of the samples that have been extracted perpendicularly. This behavior enables a comparison of these two conditions. A detailed view can be achieved by the aid of the electronic part of the thermal conductivity, according to Eq. 3.4.

Regarding the electronic part of the thermal conductivity, the alloy L2 showed the substantially highest values (Fig. 3.4 b). The non-linearity at 240°C is also present in the electronic thermal conductivity, due to the relationship with the resistivity (Eq. 3.4). Regarding the TD and RD chisels, some differences are noticeable, whereas the temperature dependent slope stays the same. The chisels in the RD were characterized by an increased electronic heat flux compared to the TD-extracted chisels. This is due to the mean free matrix path length in the matrix, which influences the

movement of the heat carriers, and therefore the thermal conductivity, significantly in heat-treatable steels [23]. Due to the parallel orientation of the carbides, the matrix free path length is significantly longer, resulting in an increased thermal conductivity, measurable through the electrical resistivity and therefore electronic thermal conductivity. Therefore, the chisel should be extracted parallel to the rolling direction and carbide orientation in order to increase heat dissipation from the cutting edge and reduce the process temperatures during woodturning due to the increased heat flux. Besides thermal conductivity, other microstructural influences would make a parallel extraction preferable. Arguably, the impact energy will increase with a parallel extraction, because the crack has to pass for a longer distance along the carbides [169, 170]. Besides this, *Berns et al.* [169, 170] showed in different studies that an increased wear resistance for the here-investigated tool steel D2 can be achieved if the mean free matrix path length is decreased. Because of the parallel alignment, the carbides are oriented perpendicular to the cutting direction, ensuring an increased wear resistance.

3.4. Conclusions

The current work describes a repurposing strategy implemented in the tool industry, where a worn-out machine circular knife was used in order to extract chisel blanks. These chisels were extracted parallel and perpendicular to the primary rolling direction, which resulted in a parallel and perpendicular carbide orientation of the chisels, respectively. Due to this, different properties were expected: the thermal conductivity was of special interest because of the expected high temperatures that occur during woodturning. Therefore, the thermal conductivity using the dynamic measurement method was measured, where the density, specific heat capacity and the thermal diffusivity were determined separately. Each parameter was therefore investigated as they vary with the measurement temperature, enabling a closer look at each factor individually. Unfortunately, it was not possible to extract samples parallel and perpendicular to the carbide direction out of the chisels for the laser-flash measurements. Therefore, an approach to calculate the electronic contribution to the thermal conductivity using the temperature-dependent measurement of the electrical resistivity and the Seebeck coefficient was used. In this way, the influence of the carbide alignment became measurable. By comparing the chisel material with the material of two conventional chisels, the thermal conductivity of the repurposed chisel was taken into perspective.

It was possible to investigate the four tool-steels independently and in a temperature-dependent manner. All parameters were identified as temperature-dependent, making a detailed knowledge of the process temperature indispensable. Nevertheless, it was possible to discover the influences on the thermal conductivity for all investigated materials. The carbide precipitation was systematically identified as the governing factor on the scattering of heat carriers, namely phonons and electrons, reducing the thermal conductivity significantly. This behavior was measurable based on the thermal and electrical conductivity, respectively. Regarding the electrical thermal conductivity, it was possible to detect an influence of the carbide orientation on the thermal conductivity. Because of the free matrix path length, the heat carriers are able to dissipate the energy better from the cutting edge, indicating that the chisel extraction should be carried out parallel to the carbide orientation.

Nevertheless, further studies regarding the wear resistance and the impact on energy consumption should be performed in future, enabling a final decision of the performance of repurposed chisels. In particular, the following observations could be made:

1. Thermal conductivity depends on the microstructure of a material, which depends on the chemical composition and heat treatment.
2. Due to the measurement temperature above the annealing temperature, the microstructure of an alloy changes, which is measurable in the thermophysical properties.
3. The thermophysical properties are also dependent on the carbide morphology.
4. Therefore, the removal of the repurposed chisel parallel to the rolling direction and, accordingly, also to the carbide orientation is to be preferred.

Chapter 4

Experimental determination of the high-temperature thermal conductivity of steel powders

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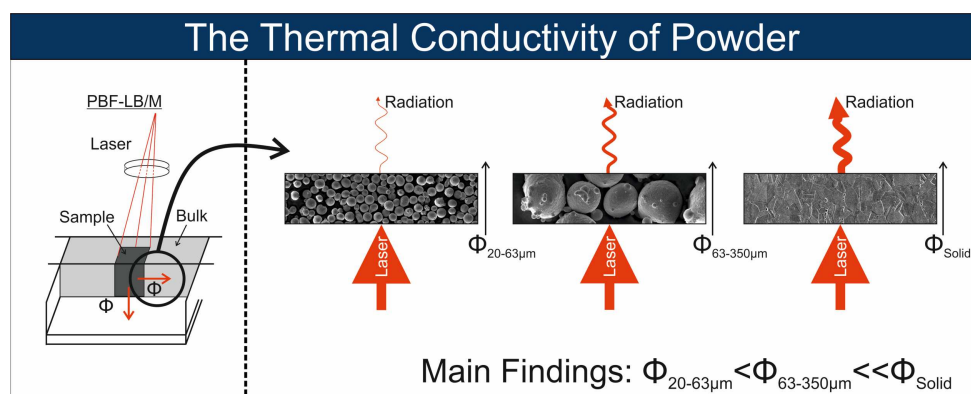
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Abstract

The PBF-LB/M process is highly suitable for the additive manufacturing of complex parts with precise geometrical accuracy using metallic powders. However, certain unknown variables exist within the process. Particularly, the thermal conductivity introduces a significant level of uncertainty due to the substantial impact of heat transfer from the part solid to the bulk material. Insufficient experimental data on the thermophysical properties of powder and a limited understanding of the influencing factors further exacerbate this issue. This study presents the thermophysical properties of steel powders commonly employed in the PBF-LB/M process, utilizing a newly-developed powder container for laser flash analysis. Through a quantitative comparative analysis with the corresponding solid materials, it has been demonstrated that the chemical composition and microstructure play a secondary role in determining the heat conductivity of the powder bed. Instead, it is the powder size distribution that serves as the primary parameter governing the observed behavior.

Keywords: Thermophysical Properties; Thermal Conductivity; Thermal Diffusivity; Characterization of Powder; Additive Manufacturing

4.1. Introduction

The interest in additive manufacturing (AM) has been growing constantly over the last decades [88]. AM allows the production of functional parts directly from 3D-CAD data, enabling a nearly infinite freedom in design with high geometrical complexity. This enables the production of shapes otherwise impossible to manufacture using conventional methods such as casting, forging or milling. Furthermore, AM facilitates a time and resource efficient way for processing highly customized parts without the need for specific tooling [89, 90]. Especially the laser powder bed fusion (PBF-LB/M) is considered the most suitable method of AM for intricate components made from metals, i.e., functional parts for automotive, energy, aerospace and medical applications [171]. The PBF-LB/M process is characterized by a focused laser beam which melts and densifies a powder bed selectively in order to produce a solid part layer by layer. In the past years, many different alloys have been investigated and successfully processed by means of PBF-LB/M, steadily opening new applications and industrial

sectors. Aluminum, titanium-, nickel- and iron-base alloys were investigated intensively in recent years [172–174]. For the latter system, the scientific literature mainly focuses on austenitic stainless steels, precipitation-hardening steels, maraging steels and tool steels [175].

Despite the high technological interest and material-based feasibility studies, PBF-LB/M still possesses many systemic process uncertainties associated with the powder bed, such as laser beam absorption, heat conduction, flow of the molten metal, phase transformations, thermal stress and distortion [91–95]. The laser beam absorption, for instance, depends strongly on particle size distribution and particle arrangement. In addition, the particles also affect the shape of the melt pool as well as the overall heat transfer and fluid flow [176]. Hereby, the build quality and material properties are affected significantly. As a result, the influence of the powder has to be considered for PBF-LB/M, often requiring expensive and elaborate testing in order to find suitable process parameters. Up to now, the properties of components manufactured by PBF-LB/M are mostly optimized by trial and error. This method is uneconomical, time-consuming and does not guarantee the desired properties. To reduce these testing efforts, several approaches of numerical modeling and finite element simulation (FE) of the PBF-LB/M process and powder bed have been investigated [94, 177–180]. The literature often shows inconsistent assumptions for modeling the powder bed and relies on significantly different thermophysical properties thereof. Semi-automated in-situ approaches are also used in some cases in order to simulate the resulting properties [94]. Commonly, the thermophysical powder properties for this modeling approaches are derived indirectly and empirically from the properties of dense material, the enclosed gas and their combination [181]. For specific heat and latent heat of fusion of metallic powders, this approach is applicable, but the thermal conductivity of a powder material is influenced strongly by its porosity or density [104]. Therefore, actual measurements of the thermophysical properties of powders are necessary. There are several methods for measuring thermal conductivity, such as the transient hot-wire method [182], the transient plane source method [183] and the laser flash analysis (LFA) method [184]. The measurement of thermal properties of metallic powders representing the actual condition in the powder bed during PBF-LB/M, however, reveals certain difficulties.

A commonly-used method for the determination of the thermal conductivity of a wide variety of materials and conditions is the laser flash method, allowing the indirect measurement of the thermal diffusivity [100, 101]. Due to the functional principle of measuring by laser flash testing, this method seems generally inapplicable for measuring powder materials. Therefore, several approaches were undertaken in order to

use the devices for liquids or modify the devices for metallic powders. *Ahsan et al.* [102], for instance, have placed metallic powder in a depicted and industrial standard “sample holder” with a “lid” for laser flash testing, which might result in inaccuracies due to contact resistance between sample holder, lid and powder.

In comparison, *Zhang et al.* [103] and *Cheng et al.* [104] have used powder-filled capsules for laser flash analysis, which were manufactured by PBF-LB/M and in-situ filled with powder during processing. These investigations combined FEA and an inverse approach to determine the influence of the powder capsule. With this method, they determined the influences of the capsule on the measurement signal. Then, the resulting thermal diffusivity of the powder has been calculated indirectly. Nevertheless, this approach reveals certain difficulties due to the unknown variables that have to be optimized. Further, with in-situ filling of the capsule it is accepted that the powder is co-heated, which can lead to sintering effects in the heat affected zone.

Following, there are some inaccuracies within the previous studies. This comes due to the presence of solid metallic capsules, which possess a much higher thermal diffusivity than the powders within. For this reason, in this work, the authors propose the application of a newly developed device, which is translucent to the here used frequencies of light. Hereby, the direct measurement of the powders within the laser flash method is achieved. With this setup, there is no need for additional simulations or a PBF-LB/M advice to manufacture the samples. Therefore, highly time-consuming processes and simulations are not necessary and the intrinsic uncertainties due to the many unknown variables in the inverse-method are avoided. Furthermore, the powders will only possess the actual measurement temperatures, circumventing inconsistencies due to pre-processes and enabling the determination of the actual powder-bed properties that are present in PBF-LB/M.

This work proposes that measurements in the actual material condition are necessary for an accurate representation of the material’s thermophysical properties for correct modeling and simulation purposes. Additionally, the powder’s chemical and geometrical properties have to be considered as well. Therefore, a complete powder characterization, chemical analysis and measurements of the thermophysical properties in the actual powder condition are conducted for three of the most commonly used steel grades for PBF-LB/M applications. The investigated alloys are the stainless austenitic steel X2CrNiMo17-12-2 (AISI 316L), the carbon-martensitic tool steel X37CrMoV5-1 (AISI H11) and the stainless precipitation-hardening steel X5CrNiCuNb17-4-4 (AISI 630, 17-4 PH). In this work, the authors try to answer the following leading scientific questions:

- What effect do microstructure and chemical composition of the powder particles exert on the thermophysical properties?
- In which way does the particle size of metal powders affect the thermophysical properties?

4.2. Experimental

4.2.1. Investigated Materials - Powder and Solid

Three different materials have been studied in this work as powder and conventionally produced semi-finished product (cast and rolled) in the as-delivered condition. Note that, throughout this work, we refer to the cast and rolled condition as *solid*—as opposed to powder—to make a clear distinction to the studied bulk properties. The three investigated materials were conventional and industrially employed powder and solid states with the chemical composition according to AISI 316L, AISI H11 and AISI 630. These materials are the most used powders in additive manufacturing processes and therefore of special interest in process simulations and current research [175].

4.2.2. Microscopy, Hardness and X-Ray Diffraction

Microscopic images in this work have been captured using a field emission scanning electron microscope (SEM) MIRA 3 by Tescan, Brno, Czech Republic with an acceleration voltage of 15 keV and a working distance of 15 mm. The metal powders were adhered to an adhesive carbon pad prior to SEM investigations. Images were taken before and after the laser flash measurements. This enables the investigation of oxidation and sintering effects during measurements, which could influence the measurement signals.

Samples of the solid materials have been embedded, grinded with SiC paper and were subsequently polished with diamond suspension with average grain sizes of 6, 3, and 1 μm respectively. Etching of the samples have been carried out with V2A-etchant at room temperature.

Vickers hardness tests were carried out with an automated testing device KB30S by KB Prüftechnik GmbH, Hochdorf-Assenheim, Germany in accordance with DIN EN ISO 6507-1 [165] to determine the exact condition of the solid samples. For each of the five measurements, the testing force was set to 98,07 N (HV10).

For analyzing the chemical composition, energy dispersive spectrometry (EDS) was applied using an X-MaxN 50 detector by Oxford Instruments, High Wycombe Buckinghamshire, United Kingdom, with an acceleration voltage of 15 keV at a working distance of 15 mm.

The volume fractions of the body-centered cubic (bcc) α and face-centered cubic (fcc) γ phases present in the investigated powders were determined using X-Ray Diffraction (XRD). A line-profile Rietveld analysis [123] has been carried out on the diffractograms. A lab-scale diffractometer D8 Advance by Bruker Corp, Billerica, USA, and the Rietveld analysis software MAUD by University of Trento, Trento, Italy, have been used. The diffractograms were recorded using CuK_α ($\text{CuK}_{\alpha 1} = 1.54060$, $\text{CuK}_{\alpha 2} = 1.544392$ Å) radiation, an operating voltage of 40 kV with an operating current of 40 mA, a Lynx-Eye detector, a detector divergence slip, 30° to 90° 2θ range, $0,01^\circ$ step size and 10 s measurement time per step. A Ni-filter was used to suppress CuK_β radiation.

4.2.3. Particle Size Measurement

The particle sizes of the investigated powders were determined by laser diffraction in accordance with ISO 13320 using a Mastersizer 2000 by Malvern Instruments Limited, Malvern, United Kingdom. For each powder, three individual samples were taken from the batch, automatically analyzed and averaged.

4.2.4. Thermal conductivity measurements

In this work, the thermal conductivity was measured using the indirect, dynamic measurement method. This method uses the independent and temperature-dependent determination of the specific isobaric heat capacity c_p , thermal diffusivity a and density ρ . Since all these factors are temperature-dependent, a differentiated consideration of all parts has to be made. The thermal conductivity is then calculated according to Eq. 4.1 [9, 42].

$$\lambda(T) = c_p(T) \cdot a(T) \cdot \rho(T) \quad (4.1)$$

Specific heat capacity

The specific isobaric heat capacity c_p was determined using a differential scanning calorimeter type HDSC PT-1600 by Linseis Messgeräte GmbH, Selb, Germany. After stabilizing, baseline corrections were carried out using two empty crucibles. Immediately afterward, calibration of the calorimeter was performed by placing a sapphire specimen in the measurement crucible. 100 mg of the powder batch were used, which replaced the sapphire specimen immediately after calibration. The solid material was measured using specimens with a diameter of 4 mm and a thickness of 0,5 mm, which replaced the sapphire specimen after calibration—just like in the case of the powder. These geometries and weights are needed, in order to keep the heat flow signal of the specimen as close as possible to the reference sapphire disc, ensuring a high-quality measurement and high reproducibility.

The solid specimens have been grinded by mesh 1000 SiC paper, to ensure a sufficient heat transfer between crucible and specimen. Thin platinum crucibles with an excessive thermal conductivity were used to minimize heat loss to maximize the quality of the measurement. All crucibles were tempered before the measurements to avoid reactions between sample and crucible and enable a sharp heat flow between sample and sensor.

The heat program remained unchanged between baseline, calibration and specimen measurements and consisted of a linear heating rate of 20 K min^{-1} to 773 K and a dwell time of 1 min before cooling. Measurements on solid and powder materials were done in a dynamic helium atmosphere with a constant flow rate of 12 L min^{-1} and an total pressure of 1,3 bar. Three independent test series were carried out for each investigated material.

Thermal diffusivity

Thermal diffusivity was measured using the laser flash principle, using a laser flash analyzer type LFA 1000 by Linseis Messgeräte GmbH, Selb, Germany. Solid specimens with a diameter of 10 mm and a thickness L of 2 mm were investigated after grinding

with mesh 1000 SiC paper and coating with a thin graphite layer to maximize laser radiation absorption.

The measurements of the powder materials were done by employing a newly developed container shown in Figure 4.1. This device consists of a container made from AISI316L, which is covered at the top and bottom by quartz glass discs made of Suprasil[®] 1. Suprasil[®] 1 has a transmission coefficient of approx. 94% for the wavelength of the used laser and the infrared detector and is thus transparent to the radiation, enabling a direct heating of the bulk on the one hand and a direct measurement of the temperature-time behavior on the other hand. The container was placed in the same sample holder as the solid samples. The powder containers inner diameter was selected as 10 mm, such that the laser can only hit the powder specimen and not the container itself. At the top, an opening of 8 mm diameter ensures that the detector can get a correct reading of the temperature evolution. This measurement design enables the direct determination of the thermal diffusivity of the powder material. The thickness L is determined by the spacing of the quartz glass discs, as was set, in this study, to 2 mm.

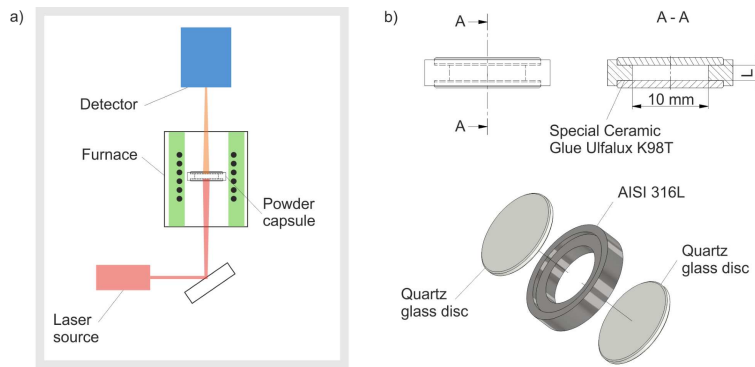


Figure 4.1.: Newly developed powder capsule for laser flash applications. a) Schematic representation of a LFA facility and the position of the developed container within it. b) Technical drawings of the powder capsule, including an explosion drawing and a diametrical cut.

The solid and powder materials were measured under a static helium atmosphere with a total pressure of 1,3 bar. For both bulk and solid measurements, the temperature of the upper side of the sample was monitored permanently through a diameter of 8 mm during and after laser irradiation. The laser spot-size, as reported by the manufacturer, is 10 mm with an energy of 27 J, respectively. Both spot-size and measurement area are smaller than the inner powder capsule diameter. To determine the lateral heat flow

and the influence of the powder-container heat transfer on the measurement signal, three FE heat flow simulations were performed in the FEA suite Abaqus CAE 2019. These comprised: (i) a model of the container geometry used, (ii) a container with 10 times the mass of the real one, and (iii) an idealized perfectly adiabatic container. In all cases, the powder quantity was defined by the receptacle dimensions in Figure 4.1 and was considered as a bulk. Note that its properties taken from our own measurements. For cases (i) and (ii), the heat transfer between the powder and the container was assumed to be perfect. All FE simulations took advantage of the symmetry of the container and were executed as axisymmetric models. We expect simulations (ii) and (iii) to provide the bounds of the error of the assumptions made regarding lateral heat flow. In (ii), the more massive container, constructed of stainless steel and glass with higher thermal conductivity and diffusivity than the analyzed powders, represents the extreme case in which the heat flow is dominated by lateral flow into the container. On the other hand, in (iii), the perfectly adiabatic assumption corresponds to a perfectly isolated capsule. Finally, simulation (i) should deliver results between these extremes, comparable to the actual LFA measurements. The thermal diffusivity was determined by the $t_{1/2}$ time which is the time required for the upper side of the specimen to reach 50% of its maximal temperature and Eq. 4.2 [46].

$$a = 1.38 \cdot \frac{L^2}{\pi^2 \cdot t_{1/2}} \quad (4.2)$$

At least three measurements on three separate specimens were executed for all investigated materials and temperatures. The average and the standard deviation were then calculated.

Density

The density of the solid materials was measured at room temperature using Archimedes' principle. These measurements were performed in air and ethanol subsequently, using a high-precision laboratory balance CPA 225D by Sartorius AG, Göttingen, Germany. The density of three different specimens was determined in three different measurements. The powder bulk densities were determined by the funnel method according to ISO 3923-1 [165]. Three individual samples were measured and averaged for each batch.

To determine the density at higher temperatures, the thermal expansion coefficient

α_{th} has to be considered, which was determined using a vertical dilatometer with an Al_2O_3 differential measurement system of the type L75 Platinum Series by Linseis Messgeräte GmbH, Selb, Germany. Round samples with a diameter of 4 mm and a length of 20 mm were investigated. The measurements were carried out in a vacuum of 2×10^{-5} Pa. The reference parameters were room temperature as well as the length of the sample at room temperature. The thermal expansion coefficient of the solid material was used to calculate the density of both the solid and powder material at high temperature. Three independent measurements on three separate specimens were performed for all materials and temperatures. The average and the standard deviation were then calculated. The porosity of the powder ϵ was calculated according to Eq. 4.3 with the solid and the powders' bulk density.

$$\epsilon = 1 - \frac{\rho_{powder}}{\rho_{solid}} \quad (4.3)$$

The average of the thermal conductivity according to Eq. 4.1 was calculated using the mean values. The standard derivation of the thermal conductivity was calculated according to the Gaussian rule of error propagation, respectively.

4.3. Results and Discussion

4.3.1. Chemical Analysis and Microscopy

To reiterate, this work focuses on the thermal conductivity on the mostly used alloys in the PBF-LB/M process [175]. These are the stainless austenitic steel AISI 316L, the carbon-martensitic tool steel AISI H11 and the stainless precipitation hardenable steel AISI 630, which have been investigated in powder and as-delivered solid condition. The chemical composition of the powders was measured by EDS and carrier-hot gas analysis and the composition of the solid materials have been measured by OES. The results are displayed in Table 4.1.

Table 4. 1.: Chemical composition of the investigated solid materials in wt.%.

	Elements	C	Si	Mn	Cr	Ni	Mo	Cu	V	Nb	Fe
Solid	AISI 316L	0.020	0.35	1.68	16.17	10.41	2.12	0.43	0.08	0.02	Bal.
	AISI H11	0.391	1.09	0.40	4.85	0.16	1.36	0.06	0.40	0.01	Bal.
	AISI 630	0.014	0.32	0.39	14.12	5.08	0.12	2.59	0.03	0.20	Bal.
Powder	AISI 316L	0.016	0.60	1.80	18.30	10.39	2.33	-	-	-	Bal.
	AISI H11	0.449	0.96	1.03	5.99	-	1.30	-	0.49	-	Bal.
	AISI 630	0.011	0.28	1.19	16.64	3.70	-	5.23	-	0.25	Bal.

The solid and powder chemical compositions do not differ significantly, just small differences are detectable due to the differing measurement procedure. The similarity in chemical composition enables a direct comparison of the measured thermophysical properties.

SEM images of the microstructures of the solid materials in the as-delivered condition are displayed in Figure 4. 2.

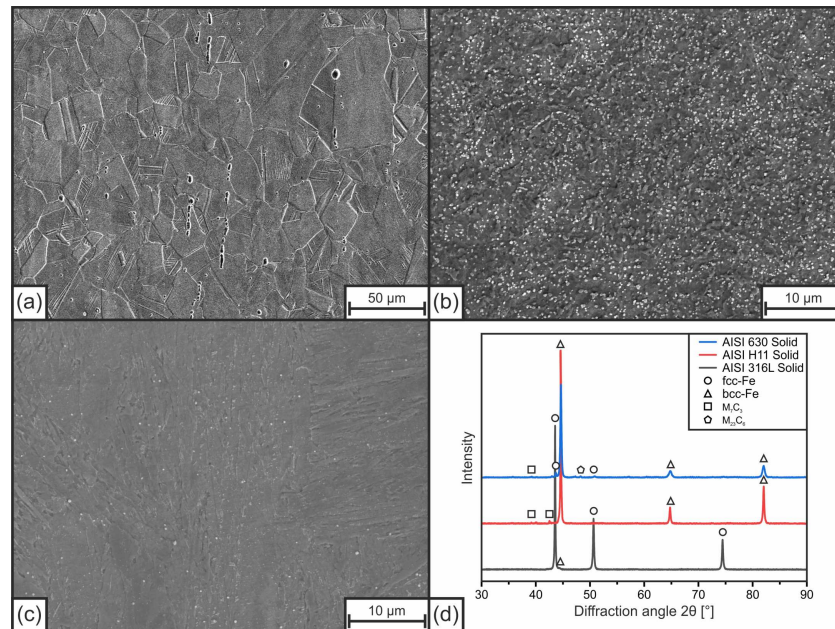


Figure 4. 2.: SEM image of the a) AISI 316L, b) AISI H11 and c) AISI 630 solid materials with the d) associated diffractogram.

Figure 4.2 (a) shows the single-phase austenitic microstructure with typical grain and annealing twin boundaries of the grade AISI 316L. Figure 4.2 (b), on the other, hand presents the AISI H11 alloy and its ferritic microstructure with carbides, namely M_7C_3 (Figure 4.2 d)). These micrographs indicate that the AISI 316L is in a solution-annealed condition and the AISI H11 is in a soft-annealed condition. In contrast, the AISI 630 in Figure 4.2 (c) is characterized by a martensitic microstructure with precipitates of M_7C_3 and $M_{23}C_6$ (Figure 4.2 d)). To evaluate the exact condition, hardness is shown in Table 4.2.

Table 4.2.: Hardness of the investigated solid materials at room-temperature.

Alloy	HV10
AISI 316L	251 ± 10
AISI H11	185 ± 2
AISI 630	392 ± 4

SEM images of the investigated gas-atomized powders are displayed in Figure 4.3. The SEM images do not show significant differences between the alloys. All investigated powders are mostly spherical, show little to no satellites and just a small fraction of irregularly shaped particles. All powders have bcc and fcc reflections in their diffractograms but show different fractions thereof.

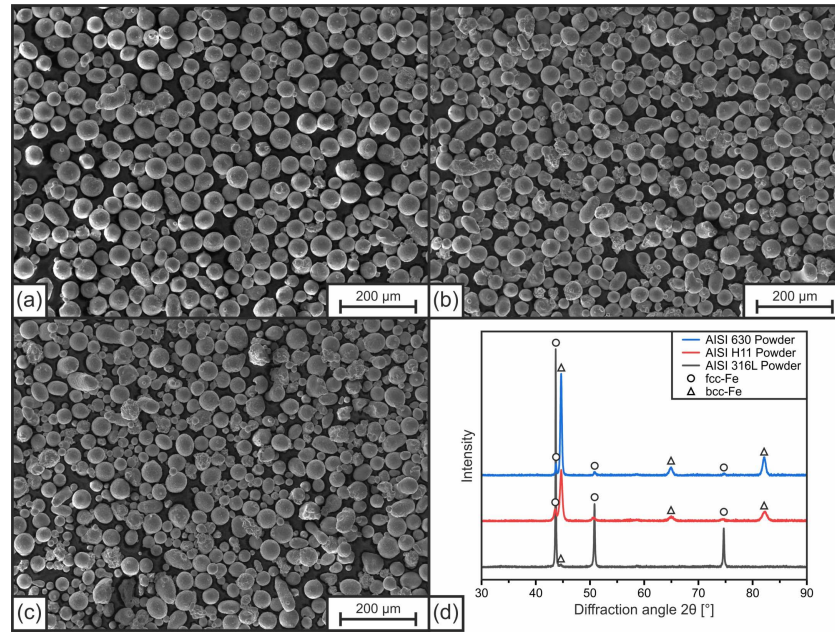


Figure 4.3.: SEM image of the a) AISI316L, b) AISIH11 and c) AISI630 powder with the d) associated diffractogram.

The phase fractions of bcc and fcc were quantified and are given in Table 4.3. The AISI316L powder is nearly single-phase fcc, whereas the AISIH11 and AISI630 are mostly bcc, with small fractions of fcc.

Table 4.3.: Volume percent of bcc and fcc present in the investigated powders obtained by XRD.

Alloy	bcc	fcc
AISI 316L	0.64 ± 0.001	99.36 ± 0.32
AISI H11	92.64 ± 0.23	7.36 ± 0.05
AISI 630	82.78 ± 0.78	17.22 ± 0.92

The particle size distributions (PSD) of the investigated powders are shown in Figure ???. The D_{10} , D_{50} and D_{90} diameters are displayed in Table 4.4. All powders show a PSD between 20 and 63 μm , with some outliers due to the irregular shape of some particles. The PSD of the AISIH11 powder is broader than the PSD of AISI316L and AISI630, which have the same mean particle diameter of 35 μm . The AISIH11 in contrast has a mean particle size of 40 μm . Nevertheless, all PSD and mean particle sizes are very

similar and can be used in PBF-LB/M processes. Therefore, the investigated powders can be considered equal in terms of morphology.

Table 4.4.: Particle sizes of the investigated powders in μm .

Alloy	D_{10}	D_{50}	D_{90}
AISI 316L	26.76	38.31	54.73
AISI H11	24.11	40.98	67.03
AISI 630	30.99	43.15	59.94

4.3.2. Thermophysical Properties

Solid Materials

Before considering the thermal conductivity of the powder materials, one has to determine and understand the thermophysical properties of the solid materials regarding their chemical composition and microstructure.

The specific heat capacity of the investigated materials AISI 316L, AISI H11 and AISI 630 as solid materials are depicted in Figure 4.5 a). All materials show a slight monotonic increase in specific heat capacity due to the full excitement of lattice vibrations [185]. The specific heat capacity of AISI 316L fits well with literature data of solid materials, making the measurements suitable for this application [186–188]. Regarding the specific heat capacity of the solids, it shows little to no differences between the studied materials. The specific heat capacity of AISI 316L is well-known in the literature and is in the range of the data presented by *Pichler et al.* [186].

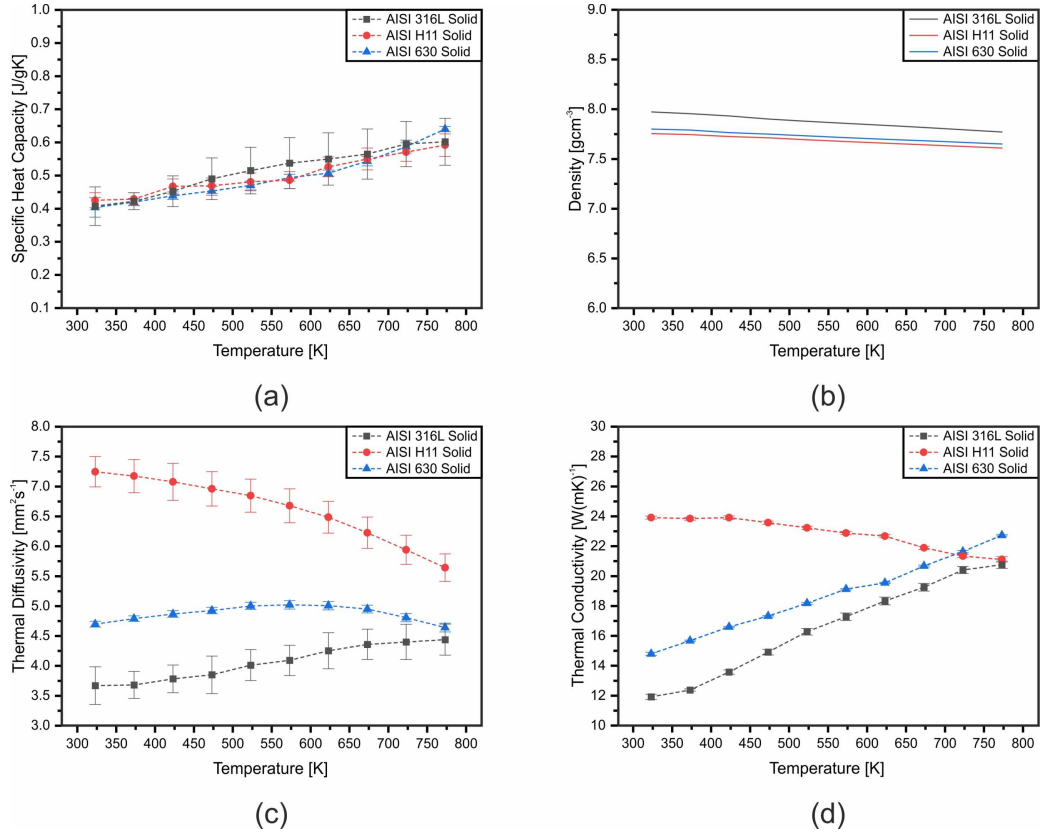


Figure 4.5.: Thermophysical properties of the investigated solid materials in a temperature range of 323 up to 773 K. a) specific heat capacity, b) density, c) thermal diffusivity and d) resulting thermal conductivity.

Nevertheless, there are some uncertainties in the DSC measurements due to the linear heating, which makes the DSC measurement delicate to control. This can be seen by comparing the measurements presented here with the stainless steel measurements performed by *Jenkins et al.* [187]. They presented a fairly lower specific heat capacity for the AISI316L alloy. The slope presented in both studies is nearly the same [186, 187]. The here-measured specific heat capacity of AISI316L lays well between the literature data. The three investigated alloys show no phase transition or precipitation effects in the investigated temperature range, which would be detectable in the DSC data [139].

The temperature-dependent density of the solid state materials is displayed in Figure 4.5 b) in a temperature range from 323 K up to 773 K. Regarding the density, an influence of the chemical composition is detectable. With increasing Cr concentration, the density decreases, which is due to the lower atomic mass in comparison to Fe and formation of Cr-carbides, that has a lower density than Fe. In contrast, heavier elements like Ni or Cu increase the density. The temperature-dependent slope is nearly

the same for all alloys, due to the rather similar thermal expansion coefficient of approx. 12 E-6/K for the AISI 630 and AISI H11 and 17 E-6/K for the alloy AISI 316L. The thermal diffusivity is the governing part of the thermal conductivity and significantly influences the time-temperature behavior of a materials, as described in the general part of the heat-conduction equation, giving it a high influence on the dynamic heat flow and thus on the PBF-LB/M process. The measured thermal diffusivities of the investigated powders obtained by the laser flash in a temperature range of 323 K up to 773 K are given in Figure 4.5 c). By comparing the thermal diffusivity of the three alloys in the solid condition, a significant difference can be observed. The AISI H11 alloy shows the highest diffusivity, which is nearly twice as high as the diffusivity of the AISI 316L alloy at RT. The thermal diffusivity of the AISI 630 alloy is slightly higher than the diffusivity of the AISI 316L alloy, when considering the RT values. These differences are due to the corresponding lattice and microstructure, which result from the chemical composition and heat treatment. The three investigated alloys differ significantly in the lattice and microstructure, which also applies to the thermal diffusivity. Due to the fcc lattice and comparatively high Cr contents, the AISI 316L grade exhibits the lowest thermal diffusivity, especially at RT.

The influence of Cr can be discussed in the context of the thermal conductivity. The thermal conductivity consists of an electronic, a phononic and a magnonic part [42, 141]. The electronic part describes the heat flux due to electrons, which contribute as heat carriers. The phononic part is due to lattice vibrations and the magnonic part is due to the orientation of magnons. The magnonic part can furthermore be neglected [42]. When one now compares the chemical compositions, a significant difference regarding the Cr content of the three alloys can be detected (Table 4.1). This difference influences the thermal diffusivity, because Cr decreases the concentration of free electrons in a Fe-base alloy due to an enhanced scattering of conduction electrons in the spin up channel [82]. This decreases the thermal diffusivity of the AISI 316L and the AISI 630 alloys.

Besides, alloying elements or carbides act as scattering sources for both the electronic and phononic parts and, therefore, decrease the thermal diffusivity and thermal conductivity [26, 141]. According to *Williams et al.* [26], alloying elements scatter especially the phonons because of induced strain fields in the lattice and mass differences between the atoms. Due to the lower concentration of alloying elements, the AISI H11 alloy is characterized by a fast heat transfer, measurable by the highest thermal diffusivity. The presence of precipitates, such as carbides in this case, increases the thermal diffusivity in comparison to a completely dissolved condition with a martensitic matrix that has a high dislocation density [34].

Taking the temperature dependency into account, one has to consider the temperature dependent slope and related effects on the thermal diffusivity. Due to a rising temperature, the concentration of free electrons increases in a high-alloyed matrix [23, 46]. This effect can be detected in the austenitic stainless steel AISI 316L. A rising temperature leads to an increased thermal diffusivity due an accelerated electronic heat flux. This is due to the direct correlation between the electronic thermal conductivity and the number of conduction electrons in a metal [42, 168]. In contrast, the AISI H11 grade shows a decrease in thermal diffusivity with rising temperature. The effect of increased phonon-phonon and phonon-electron interaction has to be taken into account, which is a result of the increased activation of phonons with rising temperature and lowers the thermal diffusivity accordingly [168].

The microstructure and chemical composition of the matrix in the AISI 630 results in a higher number of free electrons, which increases the thermal diffusivity up to 573 K. The lattice, in combination with its high-alloyed matrix, makes this alloy a middle-point between the AISI 316L and AISI H11 alloys. This is noticeable in temperatures above 573 K, where an accelerated phonon-phonon and electron-phonon scattering counteracts the further excitement of electrons, therefore decreasing the thermal diffusivity and conductivity. The resulting thermal conductivity can be calculated according to Equation 4.1 and is displayed in Figure 4.5 d). When one compares the thermal diffusivity and thermal conductivity, a substantial correlation can be derived. This can be observed, by comparing the slopes of the thermal diffusivity and conductivity. The density and specific heat capacity are rather similar between the three investigated alloys, enabling the thermal diffusivity to exert a strong influence on the conductivity. Regarding the thermal conductivity at RT of the three investigated solid materials, significant differences between the alloys were found. Due to the comparatively low thermal diffusivity, the AISI 316L alloy shows the lowest thermal conductivity. The thermal conductivity of AISI 630 is not significantly higher than the austenitic stainless steel AISI 316L due to the higher density (Figure 4.5 b)). The AISI H11 tool steel, in contrast, shows a significantly higher thermal conductivity, which results from the highest thermal diffusivity. When accounting for the temperature-dependency of the investigated alloys, break-even points can be discovered. These points result from different temperature-dependent slopes in the thermal diffusivity. Considering these, it should be clear that not only a use of RT values is sufficient, but also the high-temperature values of thermal conductivity should be considered in material modelling.

Powder Material

Following with the thermophysical properties of the powder materials, the same methodology as for the thermal conductivity of the solid materials has been used. The properties of powder will be discussed and compared with the solid materials in the following paragraphs.

The specific heat capacity of the powder is to be compared with the solid materials due to the measurement procedure (Figure 4.5 a) and Figure 4.6 a)). It can be seen that the specific heat capacities of powder and solid are similar. Small effects of the atmosphere gas can be detected due to the porosity of the powder samples. The gas has a high specific heat capacity but a low density and therefore low mass, influencing the signal just slightly. This can be observed especially at lower temperatures, where the specific heat capacities of powder and solid are nearly identical. In a direct comparison, one can observe a small error bar in the powder DSC measurement. This might be attributed to better covering of the surface area of the Pt crucible, enhancing the heat-flux between crucible and bulk.

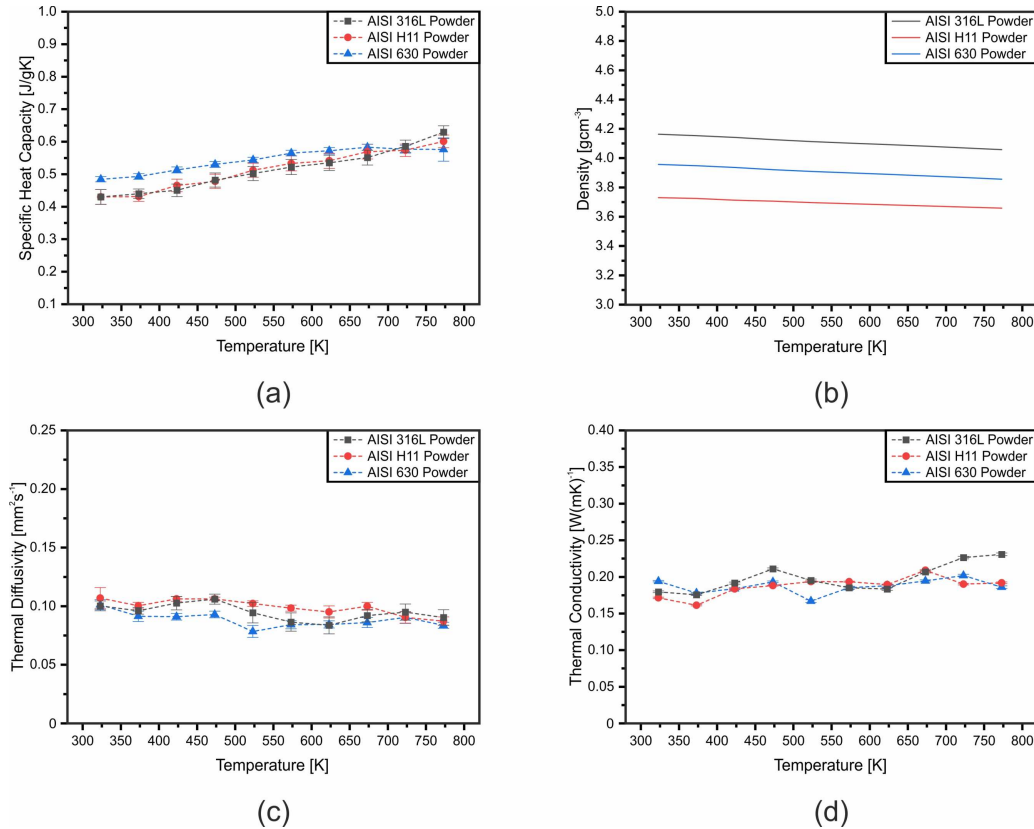


Figure 4.6.: Thermophysical properties of the investigated powders in a temperature range of 323 K up to 773 K. a) specific heat capacity, b) density, c) thermal diffusivity and d) resulting thermal conductivity.

The temperature-dependent density of the investigated alloys is displayed in Figure 4.6 b). The influences on the density can be analyzed by the porosity of the bulk (Eq. 4.3). The calculated values are displayed in Table 4.5. The porosity of the three alloys is similar, with a closer packing in the AISI630 alloy. The density at RT of the AISI316L powder is higher than the density of the AISI630 powder, while the AISIH11 powder shows the lowest density. Nevertheless, the influence of the chemical composition, that has been observed in the solid materials, has to be superimposed with the density of the bulk.

Table 4.5.: Porosity at RT of the investigated bulk calculated with Eq. 4.3.

Alloy	Porosity
AISI 316L	0.477
AISI H11	0.490
AISI 630	0.521

The thermal diffusivity has already been stated as the governing factor when it comes to the thermal conductivity of metallic alloys. Note that the measured thermal diffusivity is the thermal diffusivity of the continuum of the powder material as well as the process gas. Therefore, the thermal diffusivity of the powder materials is of special interest (Figure 4.6 c)). The measurements show a non-monotonic, temperature-dependent slope of all powders with a low influence of the rising temperature on the thermal diffusivity. The thermal diffusivity of the powder materials is similar and significantly lower than in the solid materials.

Furthermore, the laser absorption and emissivity of the powder should be noticed. The laser absorption of powder with different PSDs has been investigated by *Brandau et al.* [189]. They showed that the absorption coefficient differs slightly in the investigated PSD range. The here-measured differences in the thermal diffusivity, obtained by laser flash, are considerably larger and are therefore ruled out as a consequence of varying absorption. Additionally, the laser absorption of the powder in a PBF-LB/M process is analogous to the laser flash measurements due to the similar wave lengths that are used in the processes. Therefore, the here-published values are directly usable in a process simulation. The powder emissivity is considered as sufficient for the measurements, as the measurements from *Mohr et al.* [190] underline. Additionally, it is possible to determine in-situ temperatures during the PBF-LB/M-process via IR-

detectors and thermographic cameras, indicating that the emissivity of the powder is sufficient.

In comparison to *Zhang et al.* [103] the here-reported diffusivity is twice as low. The measured thermal diffusivity in our work is obtained directly by laser flash principle as opposed to the work by *Zhang et al.* [103]—the quartz glass discs enable a direct heating of the powder bed and the measurement of the temperature profile on the top of the powder sample (Figure 4.1). In addition, due to the low reflection of the powder, a good absorption of the laser beam is guaranteed [191]. The direct heating of the powder enables a more precise measurement and determination of the powder properties. The supporting simulations showed that the effects of the lateral heat flow could be safely neglected. The FE simulation of the 316L powder batch in the real container geometry produced a $t_{1/2}$ time within 3.2% of the measurement. Moreover, the difference in the $t_{1/2}$ time between the adiabatic and the 10x more massive container lie within the 5% uncertainty of the experimental setup, as reported by the manufacturer. As a result, the models used clearly indicate that a *shortcircuit* of the powder specimen, i.e., a heat flow dominated by the properties of the container itself, is not a concern with the current setup and LFA facility employed. The reader should check the compatibility of the proposed approach with other existing measurement facilities of other manufacturers, including a confirmation of the laser source specification, specimen holder sizes, and furnace and operation gas.

By comparing the thermal diffusivity of the powder with the solid materials, one can clearly see the differences regarding this property (Figure 4.5 c) and Figure 4.6 c)). The investigated solid materials show a strongly divergent thermal diffusivity behavior with rising temperature in comparison to the powder materials. In comparison to Figure 4.6, the solid materials show a significant difference to one another (Figure 4.5). The tool steel AISI H11 shows a decrease in thermal diffusivity with rising temperature, while the austenitic stainless steel AISI 316L increases. The solid material of AISI 630 shows just a slight change in thermal diffusivity with rising temperature. These temperature-dependent behaviors are characteristics of the lattice structures and solution conditions, which are governed by their chemical composition and heat treatment as already stated (Figure 4.2 and Section 4.3.2) [23, 34, 139]. All of these characteristics are not detectable in the thermal diffusivity of the powder. Therefore, an influence on the chemical composition or microstructure can be neglected.

The arising question "which parameters are influencing the thermal diffusivity of the powder?" is ultimately an interesting one. To answer it, the powder has to be investigated after the measurement was performed. None of the powders shows any sign of oxidization or sintering effects of the particles after the laser flash process, which can

be seen in the SEM images of the investigated powders after the laser flash process (Figure 4.7).

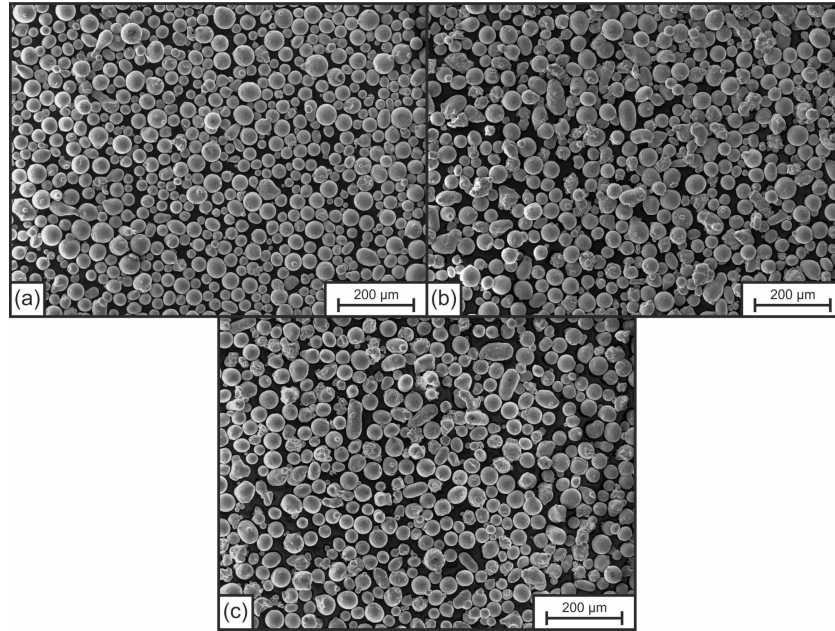


Figure 4.7.: SEM image of the a) AISI 316L, b) AISI H11 and c) AISI 630 powder after the laser flash measurement.

For this reason, the powder morphology does not change, resulting in a comparatively constant thermal diffusivity with increasing temperature. As the powder morphology stays unchanged during the measurement, it can be compared with the solid measurements. Therefore, the powder morphology, which is the same for the here characterized powders, is the major influencing factor when it comes to the thermal conductivity. The contact resistivity between different powder particles might hinder the heat flux through the bulk, reducing the thermal diffusivity sharply. Furthermore, the high contact resistance could suppress the significantly faster heat flux through the particle, which is influenced by the microstructure and chemical composition. Therefore, no correlation between the solid and the powder thermal diffusivity can occur. To underline this, fewer contact points, which come through bigger particles, might increase the thermal diffusivity. Further results regarding this hypothesis will be given in Section 4.3.3.

The resulting thermal conductivity of the powder materials is displayed in Figure 4.6 d). The uncertainties of the thermal conductivity are mainly governed by influences of the thermal diffusivity, due to the opposing but continuous slope of density and specific

heat capacity. The values of the thermal conductivity do not differ significantly with rising temperature. *Wei et al.* [192] showed a similar slope for the thermal conductivity of powders, while they measured with a hot-bridge method at lower temperatures, preventing the breakdown of the thermal conductivity into the various influences [192]. Besides the slope, the thermal conductivity shows slightly different values than shown here, which might correlate with the different particle size that was not presented in their study [192].

The work by *Rombouts et al.* [99] also presents intriguing results that are relevant to this study. However, their values for AISI 316L indicate lower effective thermal conductivities. This is most likely attributed to their measurement setup, particularly the measurement in air, which could be problematic in this context and might yield different results, as demonstrated by *Wei et al.* [192].

To conclude this section, here is a brief summary of the presented results: The measured thermal diffusivity of the powder material used in PBF-LB/M is significantly lower than the diffusivity of solid material (Figure 4.6 c) and Figure 4.5 c)). This behavior can be attributed to the limited heat transfer through the particle interfaces. As already mentioned, the solid materials show a temperature-dependent behavior, which cannot be detected in the powder materials. This behavior can also be seen in the thermal conductivity, which is determined by the diffusivity of solid and powder, respectively (Figure 4.5). In comparison with the powder's thermal conductivity the solid material shows significantly higher values.

4.3.3. Influence of Particle Size Distribution

The thermal conductivity consists of the specific heat capacity, thermal diffusivity and density (Eq. 4.1). These parameters have been measured separately and have therefore different influences on the resulting thermal conductivity. Whereas the influence on the particle size distribution on the density is easy to understand, the differences between powder materials with different particle size distributions and solid material regarding the thermal diffusivity and specific heat capacity are difficult to predict and require a dedicated measurement. These influences should thus be analyzed in the following, especially regarding the thermal diffusivity.

Up to this point, the investigated powder materials are the fractions primarily used for PBF-LB/M with an overall particle size distribution of 20-63 μm (Figure ??). The similar thermal conductivity and diffusivity of the different powders with different

chemical compositions and the same PSD indicates that the PSD might influence the thermal conductivity and diffusivity, respectively. The photopyroelectric measurements of the effective thermal conductivity of *Rombouts et al.* [99] also showed that the bulk density influences the thermophysical properties of the powders significantly, indicating that the geometry of the powder is the main factor when it comes to heat transfer inside a bulk. Furthermore, simulations of *Mukherjee et al.* [193] also showed a similar regularity, whereas the thermal conductivity of AISI 316L powder is simulated directly. They described that the tendency of a higher thermal conductivity comes with an increased particle size. For this reason, three further powder specimens of the steel grade AISI 316L with a differing PSD were investigated by means of laser flash testing (Figure 4.9). These powders possess particle sizes between 45 - 150 μm and 63 - 350 μm . SEM images of the initial state are displayed in Figure 4.8.

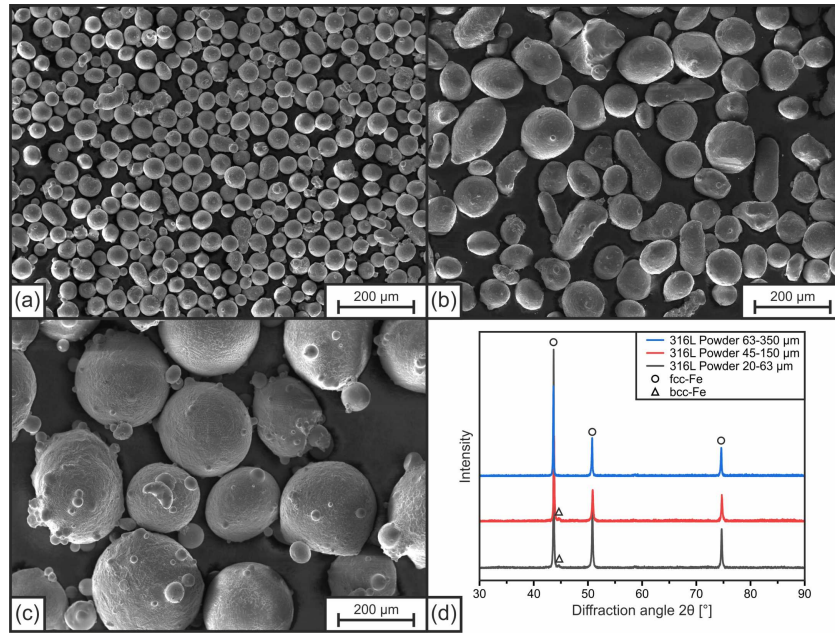


Figure 4.8.: SEM image of the AISI 316L powders with a PSD of a) 20-63 μm , b) 45-150 μm and c) 63-350 μm .

Table 4.6 displays the measured bulk density and the porosity of the investigated AISI 316L powders. The powders with a broader PSD show a higher density at RT and therefore a lower porosity, indicating a better packing of the particles. The porosity might influence the thermal diffusivity due to the dense packing.

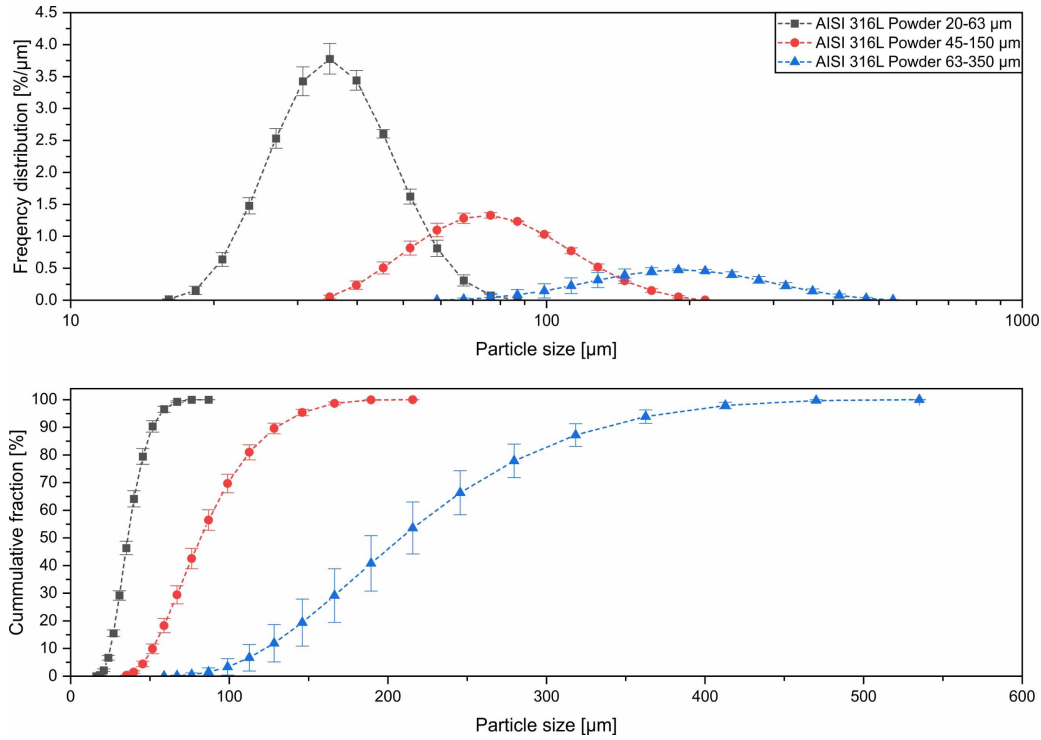


Figure 4.9.: Particle size distribution of the three investigated AISI 316L powders.

Table 4.6.: Density of the measured AISI 316L powders with different PSD.

Alloy	Density at RT	Bulk porosity
AISI 316L 20 - 63 μm	4.17 ± 0.001	0.477
AISI 316L 45 - 150 μm	4.74 ± 0.005	0.405
AISI 316L 63 - 350 μm	4.71 ± 0.142	0.408

The results of the laser flash measurements are displayed in Figure 4.10. The measurements show that the diffusivity of powders with bigger particles and a broader PSD is higher, but just shifted to higher values while the slope stays similar. With the higher particle sizes, there are similarities between *Wei et al.* [192] and the here presented results of AISI 316L with a PSD of 63 - 350 μm. Some uncertainties regarding this comparison might come through their not further specified measurement sample holder. Nevertheless, the here presented results might correlate with the latest research and can therefore be stated as accurate.

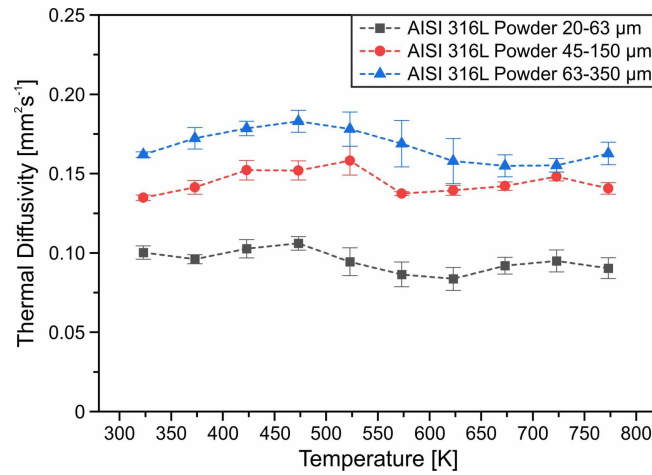


Figure 4.10.: Thermal diffusivity of the different particle size distributions of 316L powder in a temperature range of 323 up to 773 K.

The correlation between PSD and thermal diffusivity can furthermore be underlined by SEM images of the powders after the laser flash measurements (Figure 4.11). Just like the PBF-LB/M powders with a PSD of 20 - 63 µm, the powders with a broader PSD and resulting larger particles show neither sintering effects nor oxidization. Therefore, the temperature-dependent slope of the investigated powders stays unchanged during the measurements.

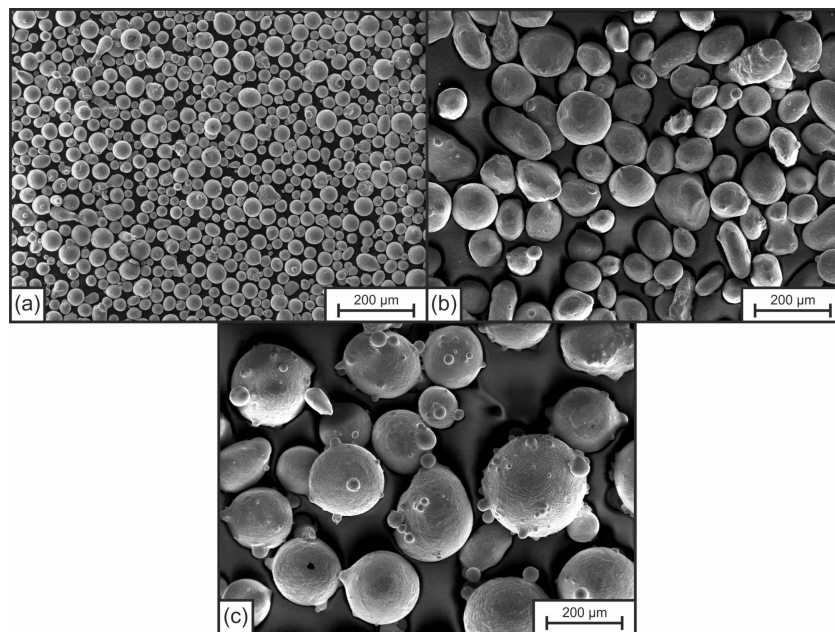


Figure 4.11.: SEM image of the AISI 316L powder with a PSD of a) 20-63 µm, b) 45-150 µm and c) 63-350 µm after the laser flash process.

The offset of the different PSDs can be explained with the particle geometry and size. Our measurements indicate that the thermal diffusivity is governed by the PSD and therefore the particle geometry. A powder with bigger particles is characterized by a higher thermal diffusivity, resulting from less contact surfaces and a faster heat transfer through the solid particle. This is due to the higher thermal conductivity of the solid material. The heat flux through contact surfaces is significantly slower than solid-state heat flux due to contact resistance, underlining this statement [97, 194]. The theoretical studies of *Gusarov and Kovalev* [98] support this hypothesis and suggest that the contact resistance plays a significant role in terms of heat conduction within a powder bed. In addition to considering the influence of the contact surfaces on the resulting bulk heat transfer, both the radiative heat transfer between particles and the gas heat transfer will be discussed in the following.

As discussed by *Wei et al.* [192], it is important to note that the contribution of heat radiation is negligible in this context, as individual powder particles exchange minimal near field radiative heat with each other [195, 196] and metals have comparatively low emissivities [45]. However, the heat conduction in the gas can vary within the beds with different PSD, thus requiring a closer examination. According to *Wei et al.* [192] and *Gusarov and Kovalev* [98], the heat transfer of the gas phase also contributes to the overall heat flow in the bulk when it comes to the thermal conductivity of a porous system. Nonetheless, these authors argue on the basis of their theoretical and experimental examinations that such heat transfer emerges from transition and free molecular transfer through the gaps in the packing [98]. It is to be noted, in this setting, that the PSD is, again, the governing factor that gives rise to these gaps in the first place. Further, it is not solely the heat flow of the gas gaps which is increased with larger particles, but a combination of increased gas heat flow and gas/solid interactions near the center of the contact surfaces [96]. Please note that in this study, we have limited the experimental examinations to one single gas environment and thus cannot derive gas-specific insights and conclusions. Nonetheless, for a set gas atmosphere, we can observe that the variable controlling the emerging apparent bulk thermophysical properties is the powder size distribution along with the specifics of the powder shapes.

4.4. Conclusions

The thermal conductivity of three different materials has been measured in the solid and powder state in a temperature range of 323 up to 773 K. The dynamic measurement method was used, enabling the distinction of influences of the thermal diffusivity, density and specific heat capacity on the resulting thermal conductivity. By means of laser flash analysis, a newly developed powder container with a quartz glass lids transparent to the wave length of the equipped laser has been used, enabling the determination of the thermal diffusivity of powder specimens. With this setup, a direct heating of the bulk and a subsequent measurement of the temperature rise at the top are enabled. Three powder materials, commonly used in PBF-LB/M processes, have been investigated regarding their thermal diffusivity, specific heat capacity and density. The powders showed similar thermophysical characteristics with little to no temperature dependency, while their chemical compositions and their phases differed. This led to the following question: Which variables influence the thermal conductivity of powder materials?

Firstly, we analyzed the thermal conductivity of associated solid materials, which have been investigated in the as-delivered condition. The thermal conductivity of the metal powder differed significantly from the conductivity of the solid materials. These differences result from the density due to the porosity of powder materials and the contrasting thermal diffusivity behavior. The specific heat capacity of both powder and solid material stayed similar. The thermal diffusivity has been identified as the governing factor of the thermal conductivity of powder and solid materials. Nevertheless, the thermal diffusivity of the solid material is strongly temperature-dependent, which is, in contrast, not the case for the powder materials. Secondly, the thermal diffusivity of the powder is furthermore influenced by the particle size distribution, due to the heat-flux through contact surfaces that is significantly slower than the heat flux within a particle due to the contact resistance and the heat transfer through the gas phase. Therefore, a larger particle size leads to an increased thermal diffusivity.

In further studies, the thermophysical properties of the powders investigated here will be evaluated at even higher temperatures to enable a better understanding of the heat-flux in hot isostatic pressing and other applications. Problems might occur due to uncontrolled sintering effects in the laser flash sample holder. Furthermore, Al- Ni- and Ti-base alloys with differing thermophysical properties will be considered. Additional experiments regarding the pressure and type of the surrounding gas will be carried out to enable a better understanding of the nature of the heat transfer in the

gas phase of the bulk.

Chapter 5

Summary and outlook

5.1. Summary

Within this work, fundamental influences on the thermophysical properties of materials across different length-scales were investigated and analysed in depth. The analysis of these properties has been carried out in three individual publications, which were written by the author of this thesis. Going more into detail, the determination of the thermophysical properties, namely thermal conductivity, consisting of the thermal expansion coefficient, density, specific heat capacity and thermal diffusivity, as well as the resistivity and Seebeck coefficient has been carried out in a broad temperature range in all the studies presented here. In these publications, the thermophysical properties of CCAs, steel powder, and tool steels have been investigated.

The objective of this work was to provide a comprehensive characterisation of the thermophysical properties of metallic materials and to gain insight into the influence of various factors at different length-scales on the thermophysical properties. By systematically investigating the influences acting on different microscopic states and materials, a comprehensive analysis of the intricate factors that underlie the thermophysical properties was carried out. To begin with the first study regarding single-phase metallic materials, only differing in their chemical composition and complexity, influences of metallic bonding, electronic structure, its correlation, and the influences on the thermophysical properties has been investigated. Interestingly, differences in the overall thermal conductivity arise from the specific heat capacity, which is strongly correlated with the metallic bonding behavior of the investigated CCAs. Regarding the

aforementioned influence of thermal diffusivity, no significant differences were found. By additional ESR measurements, SRO has been attributed in all of the investigated CCAs, as their conduction electron signal was superimposed by signals resulting from ferro- and paramagnetic atoms. Signals from these SRO effects were also detectable in the specific heat capacity of the investigated CCAs.

By comparing these results with the investigations carried out on multiphase tool steels, the influence of specific heat capacity becomes less pronounced, but the thermal diffusivity plays a pivotal role in determining the thermal conductivity. Due to the multiphase nature and the different lattice strains resulting from the martensitic matrix, the thermal diffusivity differs considerably here, which was still similar in the single-phase CCAs. Influences of rolling direction and corresponding carbide morphology and alignment were visible in the electronic thermal conductivity, showing the significant influence of second phases. Overall, a nesting strategy focusing on the extraction of tools in the rolling direction of the primary tool should be favoured.

Nevertheless, all these previously mentioned influencing factors - electronic structure, carbide orientation and shape, SRO, etc. - are intrinsic factors, revealing a strong contrast between the thermophysical properties of powders and solid materials. While microstructure and chemical composition exerted significant control over the thermophysical properties of the latter, they had negligible effects on powders. This observation holds particular importance in the context of additive manufacturing, where powder beds and their thermal management play a crucial role. Regarding the powders investigated, it has been found that the thermal conductivity of powders is markedly lower than that of solids, highlighting the critical need for accurate predictive models in additive manufacturing processes. Specifically, the most significant differences were a result from the thermal diffusivity, which differed by orders of magnitude from the corresponding solid materials. Additionally, the thermal diffusivity of the investigated powders showed similar values, regardless of their chemical composition and corresponding microstructure, indicating that extrinsic factors determine their properties. Additionally, no sintering effects were detectable, indicating no temperature dependent change in the particle geometry, showing the significance of this statement. By alternating the particle sizes, differing thermophysical properties were achievable, underlining the significant importance of the particle geometry and sizes.

All of these findings underscore the intricate interplay between intrinsic factors such as material composition, microstructure, as well as extrinsic factors such as particle sizes and shape in correlation with their thermophysical behavior, offering valuable insights for the optimization of manufacturing processes and material design strategies.

5.2. Outlook

In the exploration of single-phase CCAs, future investigations should prioritize exploring low-temperature thermophysical properties to broaden our understanding of this material family. These measurements should be coupled with corresponding ESR studies to obtain additional insights into the electronic properties as a function of temperature. Through such endeavors, it becomes possible to measure the gyromagnetic factor of CrCoNi across different temperatures, facilitating the direct calculation of the concentration of free electrons, thereby advancing our comprehension of these materials.

Given that the measured thermophysical properties of tool steels exhibit discernible differences attributed to variations in chemical compositions of the matrix, employing techniques such as Wavelength Dispersive X-ray Spectroscopy becomes imperative to further assess the microstructure of these alloys. Additionally, establishing a more nuanced correlation between wear tests and thermophysical properties is crucial. This correlation can offer deeper insights into how variations in microstructure and thermophysical properties influence the performance and durability of tool steels under abrasive wear conditions, thereby facilitating the optimization of material selection and processing techniques in industrial applications.

When it comes to the thermal conductivity of powders, the measurements presented here indicated that the chemical composition does not determine the thermal conductivity of the bulk. Nonetheless, a recent study by *Lüddecke et al.* [197] suggests that the thermal diffusivity might be influenced by the chemical composition as they showed slightly higher thermal diffusivities than presented here, challenging the presented hypothesis. Nevertheless, the presented values by *Lüddecke et al.* [197] are of a similar magnitude, indicating that the contact resistance is also predominant and independent of the chemical composition. Therefore, further studies should concentrate on the influence of the chemical composition as well as the contact surface between the powder particles, as this is of particular relevance regarding the contact resistance. Additionally, strategies to fine-tune the powder surfaces in order to establish a desired thermal conductivity could be promising, leading to improved thermal conditions while building parts. This could be achieved by alternating the morphology of the powders, such as altering particle shape or even coating the particles with materials possessing high thermal conductivity. Moreover, there is a need to attain higher measurement temperatures to gain deeper insights into the additive manufacturing process. Lastly, with comprehensive knowledge of both solid and powder thermophysical properties, it

becomes feasible to determine the contact resistance between powder and solid samples during the building process in PBF-LB/M. This endeavor not only enriches the dataset necessary for optimizing simulations but also sheds light on crucial parameters governing the additive manufacturing process.

Chapter 6

List of publications

Berger, A.; Benito, S.; Konchits, A.; Laplanche, G.; Shanina, B.; Weber, S.: "*Thermophysical properties of equiatomic CrMnFeCoNi, CrFeCoNi, CrCoNi, and CrFeNi high- and medium-entropy alloys*", in *Materials Today Communications* (2024)

Berger, A.; Egels, G.; Fussik, R.; Benito, S.; Weber, S.: "*A New Approach to the Optimization of the Austenite Stability of Metastable Austenitic Stainless Steels*", in *Journal of Materials Engineering and Performance* 32, p. 9244–9252 (2023)

Berger, A.; Ziesing, U.; Benito, S.; Weber, S.: "*Experimental determination of the high-temperature thermal conductivity of steel powders*", in *Powder Technology* 431 (2024), p. 11902

Berger, A.; Ziesing, U.; Benito, S.; Weber, S.: "*A New Experimental Investigation Of The High-Temperature Thermophysical Properties Of Metallic Powders*", in *Euro PM2023 Proceedings* (2023)

Berger, A.; Benito, S.; Kronenberg, P.; Weber, S.: "*Impact of Thermophysical Properties of High-Alloy Tool Steels on Their Performance in Re-Purposing Applications*", in *Materials* (2022), 15(23), 8702

Berger, A.; Walter, M.; Benito, S.; Weber, S.: "*Hot Wear of Single Phase fcc Materials—Influence of Temperature, Alloy Composition and Stacking Fault Energy*", in *Metals* (2021), 11(12), 2062

Lüddecke, A.; Zetzner, H.; Hantke, N.; Berger, A.; Scheck, M.; Weber, S.; Sehr, J.; Kwade, A.: "*Tailoring metal powders by dry nanoparticle coating for Powder Bed Fusion applications*", in *Powder Technology* (2024) 440, p. 119790

Kronenberg, P.; Hagedorn, W.; Berger, A.; Hellwig, F.; Wieczorek, S.; Jäger, S.; Weber, S.; Röttger, A.: "*Repurpose - How to upgrade tools and save resources*", in *Cleaner Waste Systems* 6 (2023), 100114

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Appendix A

Additional publications with first authorship

Article

Hot Wear of Single Phase fcc Materials—Influence of Temperature, Alloy Composition and Stacking Fault Energy

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Abstract: The severe sliding abrasion of single-phase metallic materials is a complex issue with a gaining importance in industrial applications. Different materials with different lattice structures react distinctly to stresses, as the material reaction to wear of counter and base body is mainly determined by the deformation behavior of the base body. For this reason, fcc materials in particular are investigated in this work because, as shown in previous studies, they exhibit better hot wear behavior than bcc materials. In particular, three austenitic steels are investigated, with pure Ni as well as Ni20Cr also being studied as benchmark materials. This allows correlations to be worked out between the hot wear of the material and their microstructural parameters. For this reason, wear tests are carried out, which are analyzed on the basis of the wear characteristics and scratch marks using Electron Backscatter Diffraction. X-ray experiments at elevated temperatures were also carried out to determine the microstructural parameters. It was found that the stacking fault energy, which influences the strain hardening potential, governs the hot wear behavior at elevated temperatures. These correlations can be underlined by analysis of the wear affected cross section, where the investigated materials have shown clear differences.

Keywords: austenitic steels; elevated temperature; high-temperature two-body abrasion; wear; hot wear; wear mechanism; electron backscattered diffraction; X-ray diffraction; stacking fault energy



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1. Introduction

The wear resistance of metallic materials at elevated temperatures is increasingly gaining traction in technology. This results in increasing requirements on the used alloys. Application examples in which high-temperature wear is the norm are construction materials used in circulating fluidized bed combustion reactors, where the structural material is engrossed by the SiO₂ carrier material at high temperature [1]. Due to this abrasive flow consisting of ceramic particles and hot carrier gas, a severe sliding abrasion of the construction material is induced [1,2].

Due to thermal softening, the alloys used for high-temperature wear applications differ significantly from the alloys used in room-temperature applications, like martensitic steels [3–6]. These steels cannot be used at temperatures above 500 °C, because the indentation of particles cannot be prevented by established room-temperature mechanisms such as martensitic hardening [3,6]. In addition, the stability of the wear-generated surface plays a significant role in the wear resistance of a material used in high-temperature wear applications [7,8]. This leads to a significant influence of the matrix material, whereas the hard phases, as used in other conventional alloys such as ledeburitic tool steels, have a negligible influence on the high temperature wear resistance because the metal matrix decisively determines the stability of the wear-induced surface [3,7–9]. In addition, the loss of support and integration of the hard phases in the metal matrix because of thermal softening mechanisms leads to an amplified material loss [3,7,9]. For these reasons, an

increased focus on the high-temperature wear resistance of the matrix material is required. In addition, fcc-phase materials are used in high-temperature wear applications because of their temperature-stable wear response in coherence to a stable wear-induced surface [4,5].

Properties associated to an increase in dynamic abrasion resistance of a material are hardness, tensile strength and especially the work-hardening capability of the matrix during deformation [3,10]. The latter in particular is able to counteract thermal softening processes at higher temperatures, making the work-hardening rate of a material essential for high temperature abrasion and stability of the wear induced surface [4,5,11].

Closely related to the deformation behavior and work-hardening capability of materials with fcc-lattice is the stacking fault energy (*SFE*). Especially in tribological systems, the *SFE* influences the wear-related properties and mechanisms, e.g., microcutting or microploughing [12]. Berns et al. [10] indicated that in austenitic steels, the stacking fault energy plays a significant role on the wear behavior and consequently on the performance of metals in high-temperature wear applications. Meanwhile, the *SFE* is a parameter influenced by metallic bonding forces, resulting from different base materials or alloy compositions as well as the temperature [13–15].

There are different ways to determine the *SFE*. It can be estimated by thermodynamic and first principle calculations, on the one hand [16–19], or it can be measured by X-ray diffraction line-profile analysis [20], weak beam techniques [21], or transmission electron microscopy, on the other hand [15,21–23]. Due to the high complexity of the experimental measurements, only few investigations can be found that focus mainly on the room-temperature (RT) measurements and values. Walter et al. [13] showed in a recent study that the *SFE* as a function of temperature can be measured in situ by X-ray line-profile analysis. Furthermore, Fussik et al. [14] indicated via thermodynamic calculations that the temperature dependent slope of *SFE* is affected by different alloy compositions.

This work focuses on the hot hardness and specific hot wear reactions of fcc-lattice metals. For this purpose, three austenitic stainless steels as well as Ni and Ni20Cr as benchmark materials will be investigated. These materials react differently to indentation and severe sliding abrasion. These reactions will be correlated to their microstructural parameters at elevated temperatures, resulting in a clear connection, which can be confirmed due to microscopic analysis in the cross section of the wear-affected zones.

2. Materials and Methods

2.1. Materials and Metallography

The high-temperature wear mechanisms and microstructural parameters of five single phase materials with fcc-lattice were investigated. Materials chosen were three austenitic stainless AISI304L/EN 1.4301 (X5CrNi18-8), AISI 316L/ EN 1.4404 (X2CrNiMo17-10-2), and X3CrNi25-20, which were optimized due to a low *SFE* slope with rising temperature by Fussik et al. [14]. To determine the effect of lattice-properties, pure Ni, as well as Ni20Cr were investigated.

The austenitic steels X5CrNi18-8 and X2CrNiMo17-10-2 used are commercially available steel grades, while the alloy X3CrNi25-20 and Ni and Ni20Cr were produced in a vacuum induction furnace (Leybold-Heraeus GmbH, Köln, Germany) using pure element-powder as well as ferroalloys (e.g., FeCr). All metals were then hot forged by a round-forging machine (Heinrich Müller Maschinenfabrik GmbH, Pforzheim, Germany) with a forging-temperature of 1100 °C. The diameter of the ingots was reduced from 42 mm to 12 mm in 10 steps. Heat treatment was done for 24 h with a temperature of 1100 °C and quenching in water. After the heat treatment, optical emission spectrometry was carried out with an emission spectrometer from OBLF GmbH, Witten, Germany. The chemical analysis is displayed in Table 1. A grain size between 30 µm and 50 µm was required to minimize the grain size influence on the wear results and hardness testing.

Table 1. Chemical composition of the investigated alloys.

Alloy	C	N	Si	Mn	Cr	Ni	Mo	Fe
X5CrNi18-8	0.03	0.07	0.40	1.65	17.91	7.98	0.23	Bal.
X2CrNiMo17-10-2	0.02	0.05	0.43	1.64	16.61	9.94	2.11	Bal.
X3CrNi25-20	0.03	–	–	–	25.5	19.5	–	Bal.
Ni	0.01	–	0.02	–	–	Bal.	–	0.05
Ni20Cr	0.01	–	0.01	–	16.87	Bal.	–	0.05

For wear and hardness testing, samples with a thickness of 4 mm were cut, grinded with SiC paper and subsequently polished with a diamond suspension with an average grain size of 6, 3, and 1 μm . Final polishing was done by oxide polishing suspension with a grain size of 0.25 μm . After testing, scar surfaces were cleaned by ultrasonic cleaning in ethanol. Wear scar subsurface regions were coated electrochemically with Ni (thickness > 20 μm) to reduce the risk of edge rounding during preparation. After coating, samples were cut in two halves exactly in the middle of the scar. The sectioning of the sample was carried out to investigate the microstructure generated by the scratch tests, which is located especially in the middle of the wear scar. The cross-sections were prepared metallographically like mentioned before, including an additional step with vibration polishing for 4 h using a silicon oxide polishing suspension with an average grain size of 0.02 μm .

2.2. Hardness Testing

High-temperature hardness testing was carried out with a high-temperature tribometer type Optimol SRV4 (Optimol Instruments Prüftechnik GmbH, München, Germany). Vickers-hardness testing was done with a modified testing device according to DIN EN ISO 6507-1/ASTM E9. The load applied was 4.903 N (HV 0.5) in a temperature range from 30 to 800 °C in 100 °C steps, a heating rate of 100 °C/min and a dwell time of 10 min. The tests were done in a forming gas atmosphere consisting of 95 vol.% Ar and 5 vol.% H₂. Hardness was evaluated at room temperature, validated with a hardness reference block and with respect to thermal shrinkage.

2.3. Wear Testing

Wear tests were done at 30 °C and from 400 °C to 700 °C in 100 K steps and a heating rate of 100 K/min, analogously to hardness testing. The tests were done with an Al₂O₃ ceramic sphere counter body (Sturm Präzision GmbH, Oberndorf-Hochmössingen, Germany) versus the steel disc base body. The Al₂O₃ ceramic was roughened by SiC abrasive paper with an average particle size of 18 μm and cleaned by ultrasonic cleaning in ethanol. The ceramic counter body oscillated over the base body with a stroke distance of 2 mm and a frequency of 1 Hz. Load was applied at the beginning with 10 N/min. During wear testing, a constant normal force of 10 N was applied for a test duration of 3000 cycles (50 min). Wear experiments were done under forming gas atmosphere (95 vol.% Ar, 5 vol.% H₂). Measurements included the friction coefficient as well as the maximal wear path, which describes exclusively the wear rate of the base material [24,25]. The conception and a more detailed description of the measurement and evaluation can be found in the work of Walter et al. [5].

2.4. Electron Backscatter Diffraction

Electron Backscatter diffraction (EBSD) measurements were performed using the MIRA3 SEM (TESCAN ORSAY HOLDING, a. s., Brno, Czech Republic) and done for selected cross-sections of the sliding wear scars. Samples were tilted for 70° and measurements were done with a detector type Nordlys nano and evaluated with the software Aztec, both by Oxford Instruments plc, Abingdon, Oxfordshire, England. The analyses were performed as mappings with hcp, bcc and fcc-iron phases included. A magnification of 2500 $\times$, an acceleration voltage of 20 kV, a working distance of 17 mm, a detector position

of 209 mm, an electron-beam diameter of 25–30 mm, a scanning step size of 60–80 nm, a binning factor of 4×4 , an exposure time of 25–40 ms, a maximum line count of 8, and a Hough resolution of 90 were selected. Furthermore, digital smoothing was carried out to minimize noise, resulting from indexing. The resulting maps are displayed as an image overlay of the band-contrast (BC) and phase distribution of the EBSD mappings and as an image of the crystallographic orientation using the IPF-Y orientation map.

2.5. Stacking Fault Energy and X-ray Diffraction

The stacking fault energy of the materials was determined by means of X-ray diffraction (XRD). Line-profile Rietveld analyses [26] were done with the diffractograms. X-ray diffractions were performed using a lab-scale diffractometer type Bruker D8 Advance (Bruker Corporation, Billerica, MA, USA) and the Rietveld analysis software MAUD (University of Trento, Trento, Italy) [13]. The diffractograms were recorded using $\text{CuK}\alpha$ ($\text{CuK}\alpha_1 = 1.54060$ $\text{CuK}\alpha_2 = 1.544392$ Å) radiation, an operating voltage of 40 kV with an operating current of 40 mA, a Lynx-Eye detector, a detector divergence slip, 40° to 55° 2θ range, 0.005° step size and 1 s measurement time per step. A Ni-filter was used to suppress $\text{CuK}\beta$ radiation. By using an energy discrimination window from 0.11 to 0.18 eV, fluorescent radiation of the Fe-based specimens was reduced. Samples were positioned directly in the X-ray line of focus and were analyzed using this setup while rotating the samples, so that the (111) and (200) reflections of the fcc-lattice were progressively detected. Each material was measured by three different samples and repeated twice for each sample.

For *SFE* measurements, it was necessary to separate powder from the bulk material by mechanical filing and subsequent sieving to a particle size ≤ 75 μm . This results in a high plastic deformation of the powder. This condition is called “cold worked” (CW). After filing, half of the produced powder was heat treated in vacuum (10^{-5} mbar) using sealed quartz glass capsules. This condition is called “annealed” (ANN). Alumina powder (grain size < 1 μm) was admixed as a standard for diffraction measurements for determination and correction of instrumental broadening.

Determination of microstructural parameters and stacking fault energy for RT and high temperature will be used as in the approach presented by Walter et al. [13] and described shortly in this section. High-temperature measurements were done with Ni as well as the austenitic stainless steels X5CrNi18-8, X2CrNiMo17-10-2, and X3CrNi25-20.

Each sample powder was mixed with Al_2O_3 powder, in order to measure sample and reference simultaneously. High-temperature experiments were carried out with the same X-ray parameters as mentioned before and used for RT-measurements, carried out on a module Type HTK16N (Anton Paar GmbH, Ostfildern-Schmarnhausen, Germany). The powder samples were positioned on a heating element, consisting of a titanium heating strip with attached thermocouples, to ensure temperature control. By using such a setup, a sufficient thickness (>1 mm) ensured the measurement of the sample only [27]. Measurements were performed in Ar-atmosphere. The starting temperature was 30°C with a stepwise increase to 50°C , 100°C , 200°C and 300°C . Cooling and heating rate were 100 K/min with a holding time of 30 min at each temperature. Specimens were measured at RT, elevated temperature and at RT after heating.

SFE was calculated from the fitted Rietveld analysis by the approach presented by Reed and Schramm [20,23]:

$$SFE = \frac{K_{111}\omega_0 G_{(111)} a_0 \langle \epsilon_{50}^2 \rangle_{111}}{\pi \sqrt{3} SFP} A^{-0.37} \quad (1)$$

The above-mentioned microstructural parameters have to be described as the following:

- $\langle \epsilon_{50}^2 \rangle_{111}$: root-mean-square (r.m.s.) microstrain in the (111) plane of the deformed fcc-lattice, from XRD;
- a_0 : lattice parameter, from XRD;

- SFP : stacking fault probability, from XRD;
- G_{111} : the shear modulus in the (111) planes [28];
- K_{111} : parameter determined by the crystal symmetry [29];
- ω_0 : uncertainties resulting from dislocation interactions [25];
- $A^{-0.37}$: correction of the elastic anisotropy [25,29].

Presented SFE values in this study were statistically calculated mean values. The results were averaged according to the principle of error propagation to determine the average SFE and the standard deviation for each material.

3. Results and Discussion

3.1. Hardness as a Function of Temperature

The hardness of a material is an indicator of its resistance against the indentation of a harder counter body, e.g., an abrasive body, representing the first stage of the abrasive wear impact. In addition, the hot hardness shows whether a material tends to unstable wear behavior at elevated temperatures. After indentation, the abrasive penetrates into the material, leading to severe abrasive wear by grooving [30]. Therefore, the ratio between the hardness of the abrasive and the base material can be used to indicate the wear rate at room temperature [31]. Particularly at high temperature, the hardness of the Al_2O_3 counter body exceeds the hardness of the base material within the investigated temperature range, showing the applicability of the measurement principle with an Al_2O_3 counter body [5,24,25].

As shown in Figure 1, the hot hardness of all materials decreases with increasing temperature. When considering Ni, it can be seen that the (hot) hardness of Ni increases significantly with the addition of 20 wt.% Cr, resulting from paraelastic solid solution strengthening [32]. Furthermore, the austenitic stainless steels showed an influence of Mo in the RT-hardness of the investigated alloys, which is limited up to 500 °C [33]. By means of high temperature hardness, no significant influence of alloy composition of the austenitic stainless steels can be pointed out. Moreover, the measured values indicate a stable hot wear behavior at elevated temperature, because no significant and not steady decrease in hot hardness can be found with rising temperature.

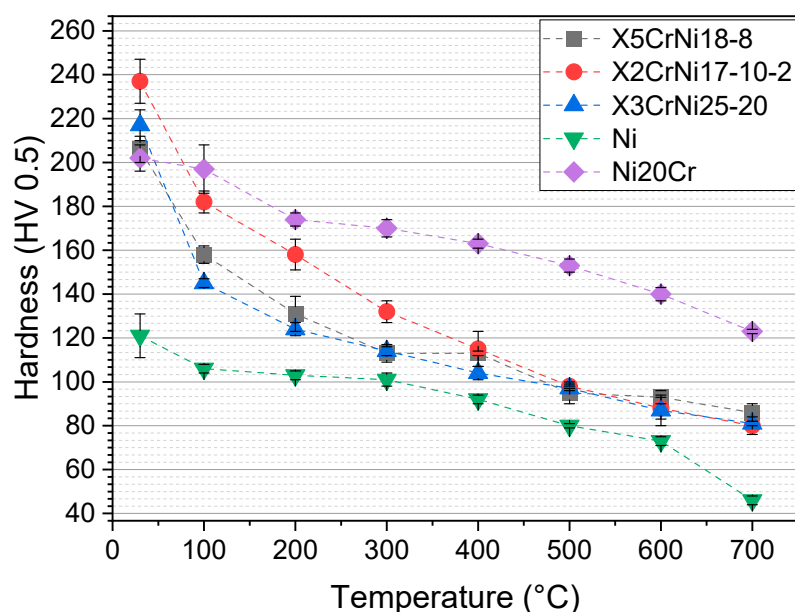


Figure 1. Temperature dependent hardness (HV 0.5) of the investigated materials.

3.2. Wear Coefficients during Sliding Abrasion as a Function of Temperature

The results of conducted sliding abrasion experiments at RT and high temperature can be seen in Figures 2 and 3. These are shown as temperature dependent friction coefficients and wear path of the investigated materials. All materials show an increase in wear rates and friction coefficient with rising temperature, which results from an increasing softening and deformability of single-phase materials. This leads to a higher lateral force during the sliding motion, resulting in a higher friction coefficient [6]. At the same time, those parameters and their dependence on temperature are strongly affected by the tested base material. Lower friction coefficients can be measured in Ni and X2CrNiMo17-10-2. Furthermore, Ni has the lowest wear path of all investigated single phase fcc materials. Ni20Cr and X3CrNi25-20 show the highest friction coefficients, indicating a higher resistance against sliding abrasion. This resistance may be due to the work-hardening capability during severe plastic deformation, which is influenced by microstructural parameters [34–36]. In terms of friction coefficient of X5CrNi18-8, the fcc-phase stability may not be sufficient, so that noticeable amounts of α' -martensite emerge during testing because of severe deformation [5]. This phase transition leads to a considerable work-hardening of this stainless steel, measured in particular by the friction coefficient [5].

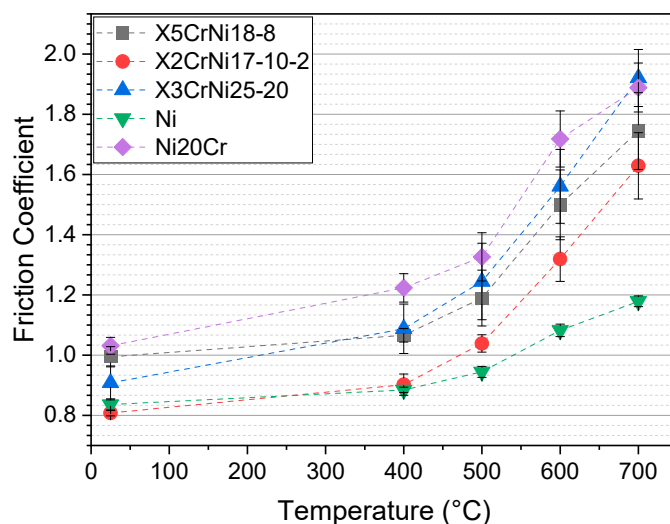


Figure 2. Friction coefficient of the investigated materials.

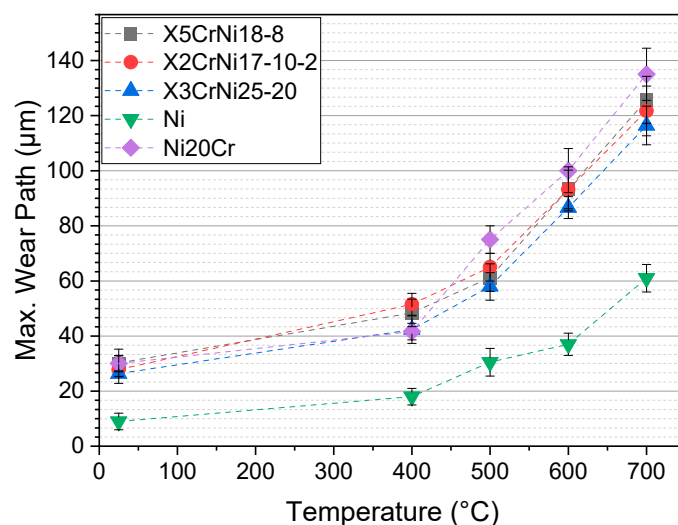


Figure 3. Maximal wear path of the investigated materials.

Especially, Ni shows a significant change in wear path and friction coefficient when alloyed with Cr. The reason for this behavior is the high ductility and low toughness of pure Ni. Therefore, it is almost exclusively plastically deformed and not ablated.

Scratch energies of the studied alloys can be seen in Figure 4, showing a lower scratch energy for Ni in comparison to the other investigated fcc materials. This parameter indicates the work-hardening potential of a material. Due to a high scratch energy describes, much energy is dissipated by microstructural deformation processes [37]. The combination of increased work hardening capability due to a lower *SFE* and the strong solid solution strengthening due to Cr increases the work required for deformation of the alloy Ni20Cr compared to pure Ni [38,39]. Scratch energy of the austenitic stainless steels resembles the scratch energy of Ni20Cr. Data shows that the austenitic steels have a breakeven point at 500 °C. This indicates that the work-hardening potential of the austenitic stainless steels is nonlinear. At 700 °C, the alloy X3CrNi25-20 has the highest scratch energy, showing that this alloy has the highest work-hardening potential, which agrees with the thermodynamic *SFE* calculations by Fussik et al. [14].

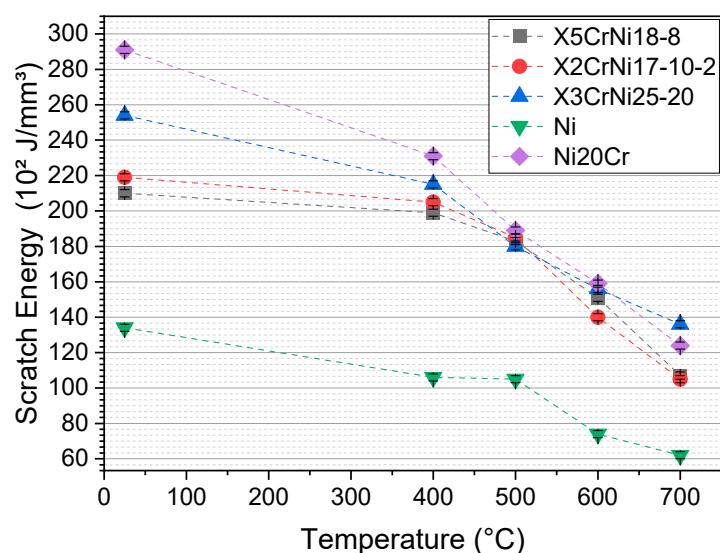


Figure 4. Scratch energy of the investigated materials.

3.3. Microstructural Parameters at Room Temperature

Table 2 displays the measured microstructural parameters of all investigated alloys at RT. The data shows that the *SFE* differs for all materials with different alloy composition. The alloy X5CrNi18-8 has the lowest *SFE*, while X2CrNiMo17-10-2 exerts a slightly higher *SFE*. X3CrNi25-20 has the highest *SFE* of the austenitic steels at RT.

Table 2. Microstructural parameters of the investigated alloys at RT.

Alloy	<i>SFP</i>	$\langle \epsilon_{50}^2 \rangle_{111} \times 10^{-6}$	a_0 (Å)	<i>SFE</i> (mJ/m ²)
X5CrNi18-8	29.49 ± 0.5	29.27 ± 0.42	3.603 ± 0.002	12.70 ± 0.9
X2CrNiMo17-10-2	18.20 ± 0.28	30.19 ± 0.29	3.606 ± 0.002	23.10 ± 1.9
X3CrNi25-20	13.40 ± 0.40	30.74 ± 0.57	3.601 ± 0.001	29.40 ± 1.1
Ni	6.71 ± 0.14	7.42 ± 0.71	3.528 ± 0.007	168.3 ± 0.7
Ni20Cr	59.40 ± 0.06	27.69 ± 0.25	3.544 ± 0.002	71.4 ± 0.9

Comparing X5CrNi18-8 and X3CrNi25-20, it can be seen that the *SFE* of X3CrNi25-20 is significantly higher at RT. This is a result of the higher Ni amount, which increases the *SFE* as well as the thermodynamic stability of the fcc phase [40]. Furthermore, Ni reduces the

volume fractions of α' -martensite of austenitic CrNi-steels in the CW condition [5,13]. The significantly higher *SFE* of pure Ni in comparison to the austenitic steels results from strong atomic bonding due to high electron density contributing to metallic bonding [29,41,42]. This correlation can be seen when the *SFE* values of Ni, Au, and Cu are compared. These elements differ in their specific lattice parameters, even though the electron density is the decisive parameter to determine the *SFE* [5,23].

Regarding Ni and Ni20Cr, the *SFE* can be lowered significantly by alloying Cr. The combination of an increased work hardening capability due to a lower *SFE* and the strong solid solution strengthening of Ni-based materials by Cr increases the work required for deformation of the alloy Ni20Cr compared to pure Ni [38,39]. This gives a direct relationship between solid solution strengthening and the *SFE* of a material, thus the formation and possibility of formation and hindrance of strengthening dislocation structures, and the material resistance to severe sliding abrasion (Figures 1–4) [43]. This behavior results from the change in electron configuration due to Cr, which in turn causes a change in binding energy, due to which the formation of stacking faults (*SF*) is significantly simplified, which can be seen in the *SFP* of both materials [44].

3.4. Influence of Microstructural Parameters and Their Behavior at Elevated Temperatures

Tables 3–5 show the temperature dependent microstructural parameters *SFP*, microstrain and lattice parameters as well as the calculated *SFE*. It is noticeable that the *SFE* is influenced by temperature and alloy composition [45,46].

Table 3. Microstructural parameters of X5CrNi-18-8 resulting from high temperature X-ray diffraction line-profile analysis.

T (°C)	<i>SFP</i>	$\langle \varepsilon_{50}^2 \rangle_{111} \times 10^{-6}$	a_0 (Å)	<i>SFE</i> (mJ/m ²)
30 _a	29.15 ± 0.029	29.29 ± 0.25	3.591 ± 0.007	12.9 ± 0.8
30 _b	29.16 ± 0.029	29.72 ± 0.25	3.601 ± 0.007	13.1 ± 0.8
50	23.50 ± 0.029	28.60 ± 0.25	3.602 ± 0.007	15.6 ± 0.8
100	12.99 ± 0.029	27.81 ± 0.25	3.604 ± 0.007	27.5 ± 0.8
200	9.17 ± 0.029	27.71 ± 0.25	3.608 ± 0.007	38.2 ± 0.8
300	5.22 ± 0.029	24.51 ± 0.25	3.612 ± 0.007	60.6 ± 0.8
30 _c	29.09 ± 0.029	29.41 ± 0.25	3.592 ± 0.007	12.9 ± 0.8

Table 4. Microstructural parameters of X3CrNi-25-20 resulting from high temperature X-ray diffraction line-profile analysis.

T (°C)	<i>SFP</i>	$\langle \varepsilon_{50}^2 \rangle_{111} \times 10^{-6}$	a_0 (Å)	<i>SFE</i> (mJ/m ²)
30 _a	13.01 ± 0.31	30.03 ± 0.39	3.601 ± 0.002	29.5 ± 1.0
30 _b	13.15 ± 0.31	30.69 ± 0.39	3.602 ± 0.002	30.2 ± 1.0
50	11.60 ± 0.31	29.70 ± 0.39	3.603 ± 0.002	33.0 ± 1.0
100	9.24 ± 0.31	28.30 ± 0.39	3.606 ± 0.002	39.4 ± 1.0
200	7.30 ± 0.31	27.77 ± 0.39	3.609 ± 0.002	49.0 ± 1.0
300	5.52 ± 0.31	26.11 ± 0.39	3.611 ± 0.002	61.0 ± 1.0
30 _c	13.00 ± 0.31	30.25 ± 0.39	3.602 ± 0.002	29.8 ± 1.0

Table 5. Microstructural parameters of Ni resulting from high temperature X-ray diffraction line-profile analysis.

T (°C)	SFP	$\langle \varepsilon_{50}^2 \rangle_{111} \times 10^{-6}$	a_0 (Å)	SFE (mJ/m ²)
30 _a	6.68 ± 0.13	7.45 ± 0.25	3.519 ± 0.004	169.5 ± 0.2
30 _b	6.70 ± 0.13	7.46 ± 0.25	3.522 ± 0.004	169.4 ± 0.2
50	6.49 ± 0.13	7.48 ± 0.25	3.524 ± 0.004	175.2 ± 0.2
100	6.03 ± 0.13	7.47 ± 0.25	3.529 ± 0.004	188.9 ± 0.2
200	5.60 ± 0.13	7.34 ± 0.25	3.535 ± 0.004	200.3 ± 0.2
300	4.23 ± 0.13	5.74 ± 0.25	3.539 ± 0.004	207.2 ± 0.2
30 _c	6.73 ± 0.13	7.51 ± 0.25	3.521 ± 0.004	170.0 ± 0.2

Regarding the *SFP*, for all materials the *SFP* decreases with increasing temperature, lowering the tendency to form planar faults. This parameter is lowest for Ni, while X5CrNi18-8 has a much higher *SFP* than X3CrNi25-20. Both stainless steels may have the same *SFP* at higher temperatures, indicating that the energy to form planar defects may be the same at rising temperature. This is due to the inverse effect of *SFE* and *SFP*, which is noticeable in these materials.

By considering the microstrain, a statement concerning the accumulated deformation can be made. The decrease of this parameter with rising temperature indicates the recovery process of the material and the rearrangement of the deformed structures take place. This is noticeable in all materials but more pronounced in the austenitic steels with rising temperature.

All materials show a thermal increase of the lattice parameter a_0 due to thermal expansion.

The increase of the *SFE* with rising temperature results from an increasing *SFP*/microstrain ratio, which increases the *SFE*. As shown by Remy and Pineau [47], the *SFE* changes at high temperatures due to the changed spacing of partial dislocations of an *SF*. When measured in situ, the *SFE* can revert to the initial value when lowering the temperature [47]. This can be observed on all alloys.

A direct comparison of the austenitic stainless steels is shown in Figure 5. When one contrasts the austenitic stainless steels, it can be stated that X3CrNi25-20 starts with a higher *SFE* value, while the *SFE* temperature gradient is lower. This behavior shows that a RT-dependent approach cannot be extrapolated to the high-temperature *SFE*, confirming the concept of alloy development from Fussik et al. [14]. Especially, a Cr/Ni-ratio of 1.25 seems optimal when comparing these alloys and when considering high-temperature low-*SFE* [14]. Meanwhile, a rising *SFE* with increasing temperature is inevitable for austenitic steels due to the thermal stabilization of the fcc phase [47]. Thus, the higher *SFE* of X3CrNi25-20 at RT states a higher austenite stability due to that correlation. Furthermore, the deformation mechanism of a material changes due to thermal reasons, which will be concretized in the following [48].

At a temperature range of 700–1000 °C, dislocation gliding is predominantly present and dynamic recrystallisation and recovery have to be considered, which are mainly influenced by the material specific *SFE* [49]. Regarding this correlation, the high temperature *SFE* is a significant parameter when developing stainless steels for high-temperature wear applications.

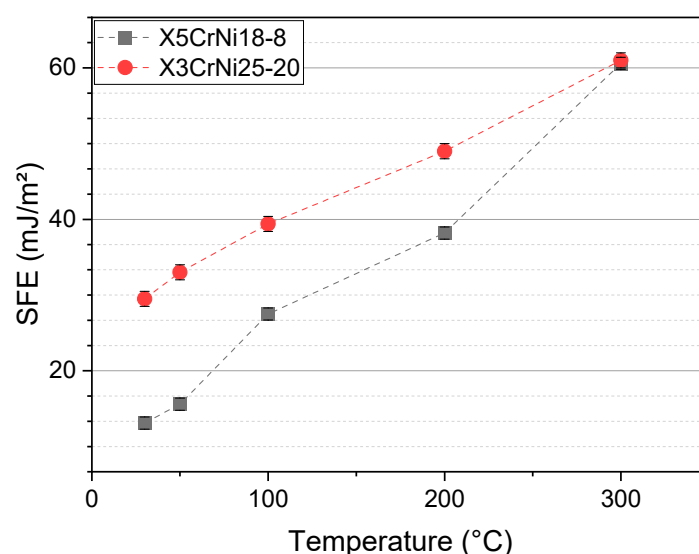


Figure 5. Temperature dependent stacking fault energy of X5CrNi18-8 and X3CrNi25-20.

3.5. Correlation of Hot Wear and Microstructural Parameters

Previous studies indicated a relationship between *SFE* and the resistance against severe sliding abrasion of austenitic stainless steels [5]. To work out the correlation, EBSD measurements of the deformed wear scars were carried out in order to determine the density of dislocation structures and dynamic recrystallisation to counteract thermal softening and indicate the work-hardening potential. Especially Ni and Ni20Cr are used, in order to determine the influence of *SFE* on the deformations mechanisms because both systems are well-known from the literature, with a well-known significantly lower *SFE* of Ni20Cr over the examined temperature range [4]. Figure 6 shows the wear affected subsurface microstructures of both Ni and Ni20Cr. The scans highlight that the material with the lower *SFE* has more pronounced dislocation structures and the area of dislocation is higher during severe plastic deformation. This indicates that the response of the material to plastic deformation by an abrasive is directly related to the *SFE* of the material. This behavior can be observed in a wide temperature range for Ni and Ni20Cr.

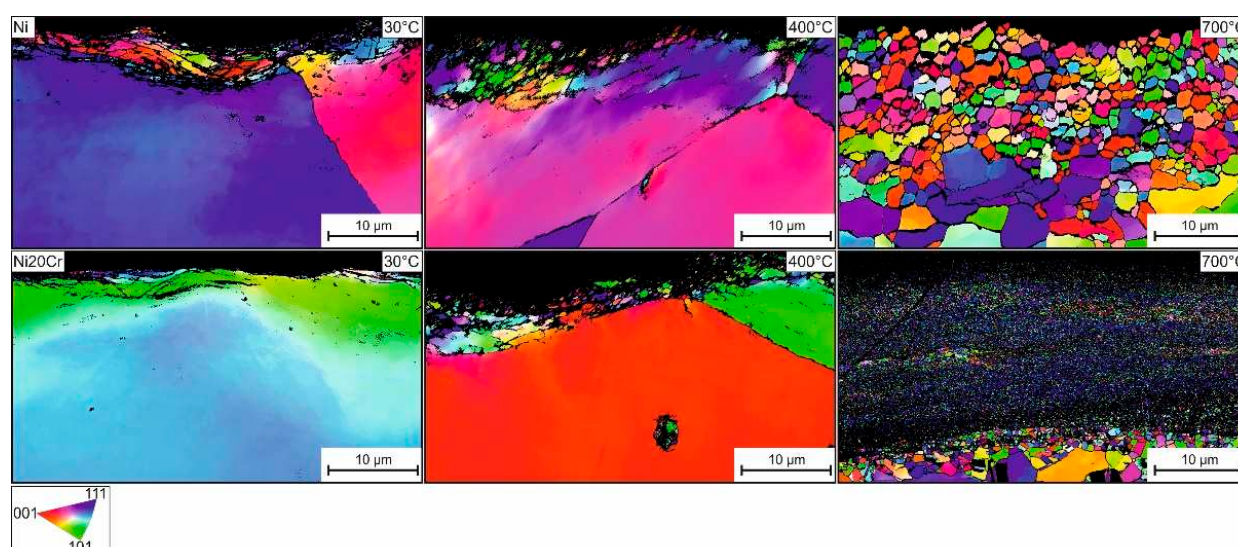


Figure 6. EBSD analysis of the subsurface microstructure of Ni and Ni20Cr. Both materials have been affected by sliding abrasion at 30, 400, and 700 °C. The cross section after 3000 wear cycles is displayed.

A similar behavior was also observed by Pinto [50] on CrNi steels. Figure 7 shows the wear-affected zone and the subsurface of the three austenitic steels X5CrNi18-8, X2CrNiMo17-10-2, and X3CrNi25-20. It has to be mentioned that for the materials X5CrNi18-8 and X2CrNiMo17-10-2, appreciable contents of α' -martensite occurred in the wear tests, which have already been investigated in a previous work by Walter et al. [5] and are therefore not part of this study. Nevertheless, all investigated alloys show a changing subsurface due to severe plastic deformation depending on temperature, while X3CrNi25-20 shows no formation of α' -martensite. The microstructural images of the wear tests at temperatures over 700 °C also show that in all the materials considered, there is a change in the microstructure as a result of thermally activated microstructural processes, from which recrystallized microstructural regions form independently of the base metal. There is a pronounced formation and extrusion of sliding band structures in the edge area of the wear marks.

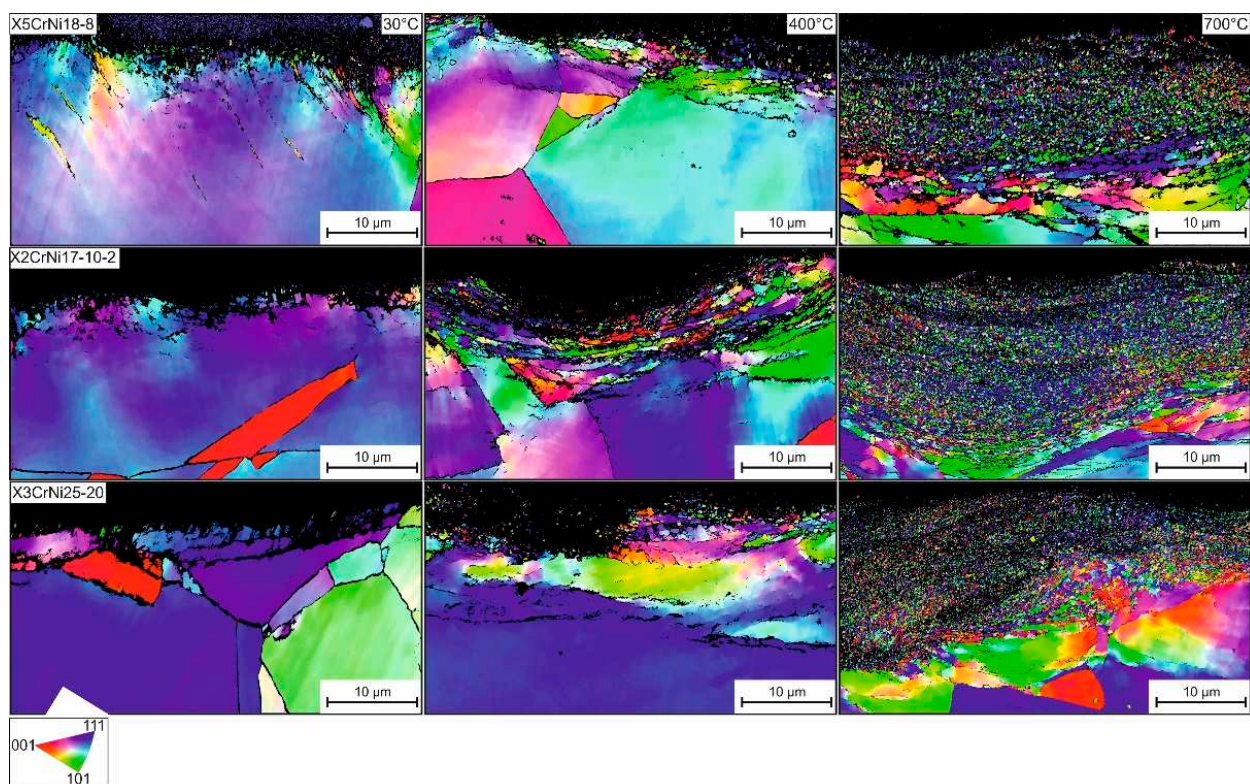


Figure 7. EBSD analysis of the subsurface microstructure of the investigated austenitic steels. All materials have been affected by sliding abrasion at 30, 400, and 700 °C. The cross section after 3000 wear cycles is shown.

This relationship between wear behavior and *SFE* becomes clear when the influence of *SFE* on the deformation behavior of fcc materials is investigated in more detail, since this deformation behavior in particular determines the response of a material to scratching. Thus, the reaction of SF with slip bands and other SF results in dislocation structures that are difficult to move. In particular, the formation of the crossing points of two SF (Lomer–Cottrell-dislocations) hinders the movement of dislocations very effectively [51]. This relationship explains why the materials with lower *SFE* react with a higher friction coefficient and a higher scratch energy (Figures 2 and 4) due to higher work-hardening capability as well as a stronger dynamic recrystallization resulting from many nucleation sites for new grain formation due to the low *SFE* (Figures 6 and 7).

4. Conclusions

This work presents the hot wear behavior as well as the microstructural parameters of three austenitic stainless steels in comparison to pure Ni and Ni20Cr. Experimental results

provide the *SFE* as a function of temperature and analyze the correlation between *SFE* and wear behavior at elevated temperatures. Particularly, the deformation behavior caused by severe sliding abrasion is analyzed as a function of temperature.

- The hot hardness tests show no instability of the mechanical properties of all fcc-materials. This is underlined by the friction coefficients and wear paths. The scratch energy shows a nonlinear correlation, with a break-even point, where the alloy X3CrNi25-20 shows a higher work-hardening potential indicated by the scratch energy than the other materials.
- In situ X-ray experiments show that the *SFE* differs significantly with an increasing temperature. The *SFE* of X5CrNi18-8 and X3CrNi25-20 differ, with a higher *SFE* of X3CrNi25-20, while both alloys have the same *SFE* at 300 °C. The reason for this behavior is the CrNi-ratio, which has been identified as a relevant parameter in previous studies and is confirmed in this work.
- The *SFE* of a material determines the work-hardening potential during abrasive sliding abrasion. Especially when considering Ni and Ni20Cr, it can be seen that the *SFE* is significantly lowered by alloying with Cr. This behavior and its impact on the hot wear behavior can be observed in the EBSD scans taken in the cross section of the wear affected area. These scans show a higher dynamic recrystallisation resulting from the lower *SFE*, which enables the material to build more SF which acts as nucleation sites for new grains. Due to the higher amount of new grains, the grain size of Ni20Cr at 700 °C in the wear affected area is significantly lower, counteracting thermal softening mechanisms.

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TECHNICAL ARTICLE

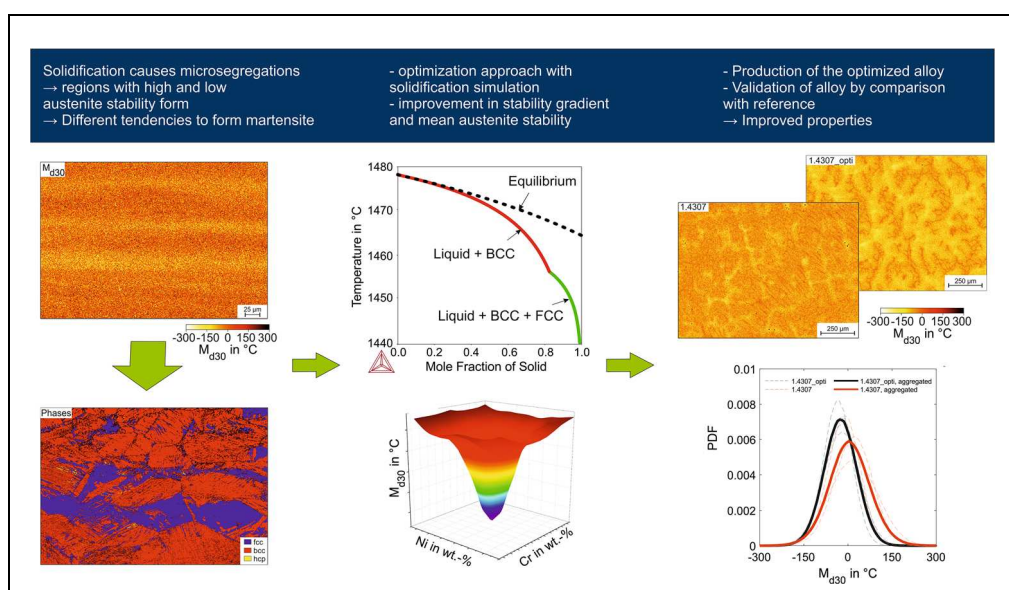
A New Approach to the Optimization of the Austenite Stability of Metastable Austenitic Stainless Steels

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Austenitic steels used for components in high-pressure hydrogen storage systems in the automotive sector have to meet high requirements in terms of material properties and cost efficiency. The commonly used 1.4435/AISI 316L type steels fulfil the technological requirements but are comparatively expensive and resource-intensive. Lower alloyed steel grades are less costly, though prone to α -martensite formation and therefore sensitive to hydrogen embrittlement. Segregation-related fluctuations of the local element concentrations exert a strong impact on the austenite stability, thus controlling the segregation behavior can improve the austenite stability of lean alloyed steel grades, making them suitable for hydrogen applications. In this work, a novel approach for the optimization of alloy compositions with the aim of improving the homogeneity of the austenite stability is developed. The approach is based on combining automated Scheil–Gulliver solidification simulations with a multi-objective optimization algorithm. The solidification simulations provide information about the influence of the segregation profiles on the local austenite stability, which are then used to optimize the alloy composition automatically. The approach is exemplarily used for an optimization within the compositional range of 1.4307/AISI 304L. It is shown that a significant increase in the homogeneity of the austenite stability can be achieved solely by adjusting the global element concentrations, which has been validated experimentally.

Graphical Abstract



Keywords austenite stability, austenitic stainless steels, CALPHAD, hydrogen environment embrittlement, simulation, solidification, optimization

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1. Introduction

The stability of the austenitic face-centered cubic (fcc) phase against thermally activated or deformation-induced transformations to body-centered cubic (bcc) martensite is a crucial aspect for the suitability of austenitic stainless steels for hydrogen applications. fcc $\rightarrow$ bcc transformations can drastically reduce the otherwise high resistance of CrNi-type austenitic stainless steels against hydrogen environment embrittlement (HEE) (Ref 1, 2). α -martensite is inherently more prone to hydrogen-induced cracking than austenite and also has a diffusivity for hydrogen atoms several orders of magnitude higher than the fcc-lattice of austenite (Ref 3-5). The latter allows a rapid accumulation of hydrogen atoms in critical sites like stress fields in front of notches or crack tips and thereby accelerates hydrogen-induced crack growth and fracture if α -martensite is present (Ref 6, 7). For this reason, HEE-resistant CrNi grades contain comparatively high amounts of Ni to provide sufficient phase stability at each position within the microstructure.

Commonly used approaches to quantify the austenite stability, and therefore also the resistance against HEE, are empirical equations for the calculation of the martensite start temperature (M_s) or the M_d -temperature, for thermally induced or deformation-induced phase transformations, respectively (Ref 2, 8, 9). Further, estimations of the austenite stability that use a thermodynamically calculated difference between the molar Gibbs energies of the fcc- and the bcc-phase, which is interpreted as a driving force for the phase transformation, can be found in the literature (Ref 10). Other authors use calculated or experimentally determined values of the stacking fault energy (SFE) as a measure for the austenite stability, as the SFE controls the formation of nucleation sites for α -martensite during plastic deformation (Ref 11-13).

In recent investigations, it has been proven that the fcc $\rightarrow$ bcc transformation is not only dependent on the overall austenite stability, that can be estimated based on the global alloy composition by using one of the aforementioned approaches, but is strongly affected by segregation-related inhomogeneities of the austenite stability throughout the microstructure due to solidification (Ref 14-16). Segregation effects of the main alloying elements in CrNi-type steels entail local minima and maxima of the austenite stability. Local minima of the austenite stability are an effect of low alloyed regions in the microstructure and facilitate local hydrogen-induced cracking upon plastic deformation in hydrogen-containing atmospheres (Ref 17-19). In high alloyed steel grades, e.g., 1.4435, which is similar to AISI 316L, comparatively low alloyed regions provide a sufficiently high austenite stability to prevent deformation-induced phase transformations and H-induced crack formation. However, that is not the case in lower alloyed and more economical grades like 1.4307/AISI 304L, which may form H-induced cracks as a result of local segregation-related phase transformations under certain testing conditions (Ref 14).

By raising the alloy content of low-alloyed regions, the local minima of the austenite stability can be increased, resulting in a reduced overall tendency to form α -martensite and hydrogen-induced cracks.

The manifestation of microsegregations in austenitic steels depends to a large extent on the exact chemical composition of the melt. The reason for this is that the chemical composition

controls the sequence of the solidifying phases as well as their equilibrium compositions (Ref 20). It is therefore possible to tune an alloy composition in a way that reduces the degree of segregation, which may improve the resistance against HEE without adding significant amounts of alloying elements. Thus, an optimization of the segregation behavior of austenitic stainless steels like 1.4307, which have a lower overall alloy content compared to 1.4435, can possibly improve their hydrogen compatibility and allow a substitution of 1.4435 steels in hydrogen applications.

The present work describes a novel, simulation-based method to optimize the chemical composition of an austenitic stainless steel with the aim of achieving a high and homogeneously distributed austenite stability. The method combines solidification simulations based on the Scheil–Gulliver equation to predict element segregation with different calculation approaches for the austenite stability and a multi-objective optimization algorithm. In order to validate this approach, the description of the method is exemplary used for the optimization of a 1.4307 steel grade within its compositional limits.

2. Methods

In the context of this work, with the aid of the TC-Python Software Development Kit (SDK) of the Thermo-Calc Software, an approach to a new concept of alloy optimization is developed, focusing on the conception of the program as well as the optimization and validation of an alloy system. To that end, solidification simulations are automatically performed in the Scheil module of Thermo-Calc, from which data of the concentrations of the individual elements along the solidification profile are transferred to Python. These concentrations provide the basis for the calculation of the objective functions. In addition, laboratory-scale ingots are produced and characterized, to review the optimization as well as the optimized alloy, which has been developed in the optimization process.

2.1 Modeling

2.1.1 Thermodynamic Modeling. The thermodynamic simulations are carried out using the 2019b version of Thermo-Calc with the TCFe9 database. Thermo-Calc is integrated in the optimization scheme, which is programmed in Python version 3.8.0, importing the libraries *numpy*, *math* and *TC-Python*. The Scheil simulations start at a temperature of 2273 K. The check for a miscibility gap is not carried out and back diffusion of C was not allowed, due to restrictions in the *TC-Python* module. The alloy contents are varied within the ranges according to Table 1 in steps of 0.25 weight percent, which corresponds to a full factorial experimental design. After the calculation of the objective functions for each of these points, the optimized alloy has been identified regarding the criterion for an optimization on the Pareto-front.

2.1.2 Objective Functions. **2.1.2.1 Targets and Restrictions.** As previously described, depending on the chemical segregation degree, the global austenite stability might be an insufficient descriptor of the local resistance against HEE. Therefore, a local description is needed to optimize the resistance against phase transformations and HEE (Ref 14,

16, 21). Accordingly, the following targets have to be achieved:

- Maximize the overall level of the austenite stability
- Minimize the stability gradient

For an optimization, these targets are to be formulated as mathematical expressions, so-called objective functions. Thus, three different metrics are used to assess the austenite stability. The three mathematical expressions applied are the M_s -temperature according to Eichelmann and Hull (Ref 22),* the M_{d30} -temperature by Nohara et al.** (Ref 8), and an equation for calculating the stacking fault energy by Qui-Xun et al.† (Ref 23). This multi-objective optimization with three independent objective functions leads to an optimized system in all parameters on the Pareto-front (Ref 24, 25). The here used empirical formulations for the optimization are used because they represent the thermally induced and strain induced martensitic transformation. Furthermore, the usage of a formulation for the SFE enables the perspective of considering ε - as well as α -martensite, making the optimization procedure more precise.

The above-mentioned stability parameters are automatically calculated for every element concentration along the solidification curves simulated with the Scheil module. Each stability curve resulting from a solidification curve provides one minimum and one maximum value of each stability parameter. This enables the algorithm to compute the minimum austenite stability (M_{d30} -maximum, M_s -maximum, SFE-minimum) and the difference between maximum and minimum austenite stability (δM_{d30} , δM_s , δSFE). With this approach, it is possible to maximize the austenite stability by minimizing the stability gradient and shifting the mean austenite stability of the microstructure to higher values.

2.1.2.2 Multi-Objective Optimization. Since the problem at hand is a multi-objective optimization, a suitable formulation must be chosen to summarize the objective functions and to find an optimal solution on the Pareto-front. The approach in this work is based on the method of distance functions with standardization of distances (Eq. 1).

$$p[f(x)] = \sqrt[r]{\left| \frac{f_i(x) - y_i}{y_i} \right|^r} \quad (\text{Eq 1})$$

In this equation, $p[f(x)]$ is the objective function resulting from the objective functions $f_i(x)$ with the respective level of demand y_i . Furthermore, the exponent r has to be varied to assure that the summary objective function $p[f(x)]$ does not depend on a single objective function $f_i(x)$. The levels of demand are defined as described in Eq. 2.

$$y_i(f_i) = |f_i(x = x_{\text{maxima}})| + \left| \frac{f_i(x = x_{\text{maxima}}) - f_i(x = x_{\text{minima}})}{f_i(x = x_{\text{maxima}})} \right| \quad (\text{Eq 2})$$

$f_i(x = x_{\text{minima}})$ corresponds to the minimum of the objective function while the maximum is described by $f_i(x = x_{\text{maxima}})$.

* $M_s = 1305 - 2667 (C + N) - 41.7 Cr - 61.1 Ni - 27.8 Si - 33.3 Mn - 36.1 Mo$.

** $M_{d30} = 551 - 462 (C + N) - 9.2 Si - 8.1 Mn - 13.7 Cr - 29 (Ni + Cu) - 18.5 Mo - 68 Nb - 1.42 (\text{grainsize}[ASTM] - 8)$; The grain size will be neglected for the optimization.

† $SFE = SFE_{FE} + 1.59 Ni - 1.34 Mn + 0.06 Mn^2 - 1.75 Cr + 0.01 Cr^2 + 15.21 Mo - 5.59 Si - 60.69 (C + 1.2 N)^{0.5} + 26.27 (C + 1.2 N) * (Cr + Mo + Mn)^{0.5} + 0.61 (Ni * (Cr + Mn))^{0.5}$.

Table 1 Restrictions (upper and lower boundary conditions) in weight percent, based on the compositional range of 1.4307

	Cr	Ni	Mn	Si	Cu
Lower boundary	17.5	8	0	0	0
Upper boundary	19.5	10.5	2	1	1

This novel optimization design allows an optimization in an objective manner, since the quality of the solution by the method of distance functions strongly depends on the level of demand (Ref 25).

For the sake of achieving an optimized alloy composition within the compositional range of 1.4307 type steel, restrictions of the system 1.4307 are used, as shown in Table 1.

In addition, Fe is balanced and C is fixed at 0.03 weight percent. Trace elements like P, S and N are not considered. The optimization led to an optimized system, which will be characterized and validated in the following, by comparing the optimized system with a reference alloy out of the commercial heat of the austenitic stainless-steel grade 1.4307–X2CrNi18-9.

2.2 Experimental Validation

The optimized alloy was produced a 200 g ingot in a vacuum induction furnace by Leybold-Heraeus GmbH (Cologne, Germany) in a 500 mbar Ar atmosphere. The reference alloy 1.4307 was produced by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG (Witten, Germany) by continuous casting and has been remelted under the same conditions as the optimized alloy. Chemical analysis of the investigated alloys is carried out by optical spark emission spectrometry (OES) using a QSG 750 by OBLF GmbH (Witten, Germany).

The ingots were solution-annealed at 1050 °C for 4 h in an argon atmosphere and quenched in water to reduce the δ -ferrite contents of the as-cast states.

For the investigation of the local element distributions and local stability parameters, specimens extending from the edge to the core of the ingots were metallographically prepared. The local element distributions were determined by means of energy-dispersive x-ray spectroscopy (EDS) using a MIRA 3 scanning electron microscope (SEM) by TESCAN ORSAY HOLDING, a.s. (Brno, Czech Republic), equipped with an X-Max 50 EDS detector by Oxford Instruments plc (Abingdon, England). The SEM was operated with an acceleration voltage of 20 kV and a working distance of 15 mm. Four EDS maps were recorded at different sites of each sample. The EDS maps cover an area of $1100 \times 820 \mu\text{m}$ each, and were recorded with a point-distance of $1 \mu\text{m}$ and a dwell time of 45 ms at each point. The acquired EDS data was subsequently quantified and exported as ASCII datasets. The ASCII datasets were used to calculate M_s , M_{d30} and the SFE for each datapoint of the EDS maps using MATLAB R2019b, resulting in two-dimensional distribution maps of the aforementioned parameters (Ref 26). As the local concentrations of the elements C and N cannot be quantitatively measured via EDS, the distribution of these elements was assumed to be constant with the concentration measured via OES.

The empirical equations for M_s , M_{d30} and SFE were previously used as objective functions for the optimization algorithm and are now adopted to assess the austenite stability distribution throughout the microstructure via EDS Mappings. In order to quantify the homogeneity of the austenite stability, the local values of the austenite stability measures were plotted as histograms. The sample mean μ , sample standard deviation σ , and mean absolute difference MAD were computed. The first parameter sheds light on the degree of the austenite stability and the other two, on its homogeneity. In particular, a lower mean value μ of M_s and M_{d30} implies higher stability, while a lower mean SFE values indicates a compromised austenite stability. Conversely, for all stability parameters, a low standard deviation and mean absolute difference point to a high homogeneity of the austenite stability—ultimately, both are dispersion descriptors of the selected measures. Equation 3, 4 and 5 display the measure definitions employed

$$\mu = \frac{1}{N} \sum_{i=1}^N X_i, \quad (\text{Eq 3})$$

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \mu)^2}, \quad (\text{Eq 4})$$

$$\text{MAD} = \sum_{i=1}^n \sum_{j=1}^n f(x_i) f(x_j) |x_i - x_j|, \quad (\text{Eq 5})$$

where N is the number of elements in the mappings, X is a placeholder symbol for the stability metrics used, i.e., M_s , M_{d30} or SFE. $f(x_i)$ is the probability density normalized histogram value at x_i , such that $i = 1, 2, \dots, n$. In other words, n is the number of bins of the histogram $f(x)$ defined by the edges x . MAD complements σ as a dispersion measure because it is nothing other than the expected absolute property difference between any two randomly chosen points. Since $n \ll N$, Eq. (5) is much faster to compute than all the pairwise absolute differences in all maps.

3. Results and Discussion

3.1 Optimized Alloy

Table 2 contains the composition resulting from the optimization (target value) as well as the measured compositions of the ingots of the optimized alloy 1.4307_opti and the reference alloy 1.4307. The target composition reveals that the Ni content ran up against the upper boundary of the allowed range, while Cr and Mn contents ran against the lower boundary. The contents of Si and Cu show that the objective function has a local minimum within the allowed range.

The actual and the target composition of 1.4307_opti do not differ significantly. The produced 1.4307_opti ingot contains only small amounts of Mn, P, S, Mo and N due to impurities in the pre-alloys that were used. Accordingly, a high degree of agreement between the solidification behavior of the target and actual composition can be assumed. The reference alloy 1.4307 in comparison is alloyed with more Mn, Mo and N as well as less Ni.

3.2 Experimental Validation

An experimental validation is needed to verify the properties of the optimized alloy and the success of the optimization process. Figure 1 displays SEM images and the qualitative local distributions of the alloying elements of the investigated alloys in two of the recorded fields.

The EDS maps display an uneven distribution of the alloying elements resulting from the solidification. The element distributions of Cr and Ni show the most significant local variations in both materials, displayed with brighter or darker color shades. This can be related to the high global alloying quantities. Si shows smaller differences due to its low global quantity. The Mn mapping of the reference alloy evidences the presence of MnS inclusions, whereas in the optimized alloy, the local variations are minimal. Due to the presence and importance of Mn in technical alloys, the influence of Mn on the optimized system has to be pointed out (Fig. 2).

Figure 2 shows the influence of a variation of Mn on the segregation behavior of the taring elements. Generally speaking, an increase of alloying elements which favor a primarily fcc-solidification (Ni, Mn, Cu, C, N) decrease the degree of segregation of one another (Ref 20, 27). Therefore, the alloying of Mn does not significantly influence the segregation behavior of the taring elements, except for Cu. Nevertheless, Cu is only alloyed in small quantities. The increased segregation of Cu can therefore be seen as non-critical.

In both materials, minor contents of δ -ferrite appear to be present in regions with particularly high Cr and low Ni contents. In both alloys, an overall tendency for the enrichment of Ni in Cr-depleted regions is visible. The contrary segregation behavior of Cr and Ni is known from primarily ferritic solidifying austenitic steels and can also be considered here. The equilibrium concentration of Cr in a primarily solidifying bcc phase lies usually above the global Cr concentration of the melt, whereas the Ni concentration in the solidifying bcc phase is usually lower (Ref 28). Consequently, the melt is being depleted with Cr and enriched with Ni, which leads to the precipitation of fcc phase from the melt at some point, making the latter solidify Cr-poor and Ni-rich. Subsequent diffusion processes combined with bcc $\rightarrow$ fcc transformations mitigate the resulting local composition gradients. Nonetheless, the contrary segregation tendencies persist in the solution-annealed condition. Pronounced contrary segregation effects do not necessarily result in strong gradients of the austenite stability; according to the equations of M_s and M_{d30} , all alloying elements contribute to a stabilization of the austenite. Contrary to the case of collective segregation effects of all alloying elements, contrary segregation tendencies can balance their local effects on the austenite stability to some extent and can therefore be regarded as beneficial for a homogeneous stability distribution. Figure 3 exemplary shows M_{d30} -maps of the investigated alloys (a) 1.4307 and (b) 1.4307_opti together with (c) histograms showing frequency distributions of the displayed data normalized by probability density.

While Fig. 3 (a) and (b) does not show obvious differences regarding the mean M_{d30} value as well as the homogeneity of M_{d30} , the histograms reveal improvements of both these properties in case of 1.4307_opti. The mean value of M_{d30} in alloy 1.4307_opti is shifted toward lower temperatures, indicating a more stable austenite on average. Also, the histogram shows a narrower profile, which means that the standard deviation will be smaller and thus the distribution of the

Table 2 Target and measured composition of the optimized alloy in wt.%. As a reference, the composition of the reference material is shown as well

	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N
Target value	0.03	0.5	0	0 (fixed)	0	17.5	10.5	0 (fixed)	0.75	0 (fixed)
1.4307_opti	0.012	0.519	0.058	0.01	0.004	17.12	10.2	0.018	0.78	0.008
1.4307	0.021	0.671	1.949	0.03	0.028	17.93	8.54	0.3	0.594	0.04

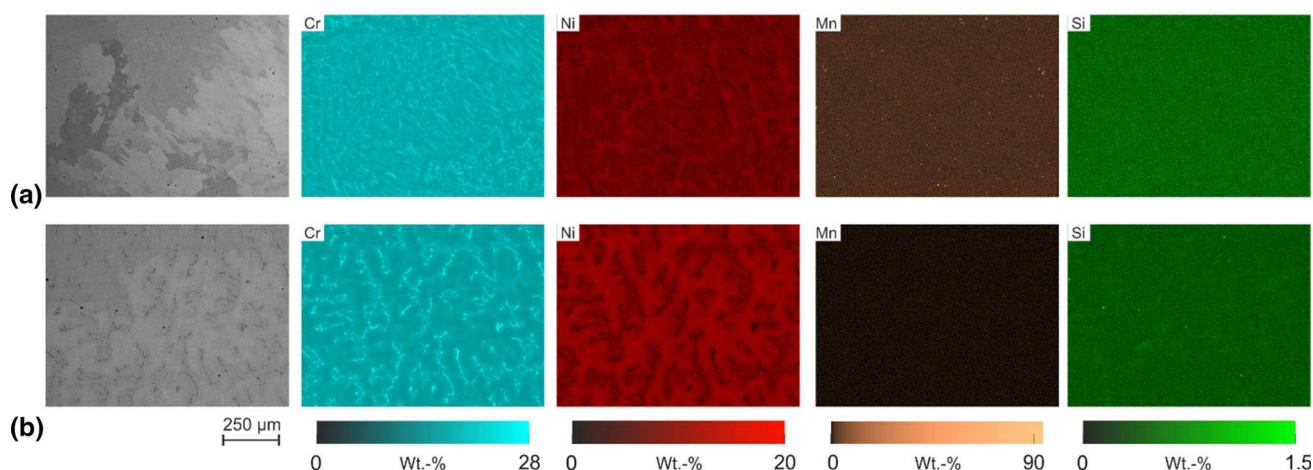


Fig. 1 Exemplary SEM images and qualitative local distributions of alloying elements in (a) 1.4307 and (b) 1.4307_opti

austenite stability is more homogeneous. A narrower histogram of a stability parameter which is shifted to a lower temperature indicates a higher, more homogeneous austenite stability.

In the same fashion as in Fig. 3 (c), Fig. 4 presents the probability density distributions of M_s , M_{d30} and the SFE for the alloys 1.4307 and 1.4307_opti. Note that fine lines correspond to the individual specimens #1-#4 and broad lines to their aggregation. Table 3, on the other hand, provides their mean values μ , their standard deviations σ , and mean absolute differences MAD, together with a relative difference calculation. Note that while the M_s and M_{d30} temperatures are presented in °C, for the computation of the relative differences between reference and optimized alloys the absolute temperature was used.

The presented data allow a comparison of the austenite stability in different locations of each ingot. It shows that there is some scattering between the data from different sites that were investigated. Scattering of μ can be explained by macro-segregation effects in the ingots, whereas the scattering of σ and MAD is most probably a result of local differences in the cooling conditions during solidification. The cooling rate especially influences the dendrite arm spacing, which defines the length scale of segregation structures (Ref 29). The smaller the length scale of the segregation structures, the faster the homogenization can occur during solution annealing. Therefore, sites with a small initial dendrite arm spacing can be assumed to have a more homogeneous distribution of the austenite stability in the annealed state.

Overall tendencies and differences between the two considered alloys can be evaluated best by comparing the probability density distributions (Fig. 4) and the corresponding sample parameters (Table 3) of the aggregated data of each alloy. The

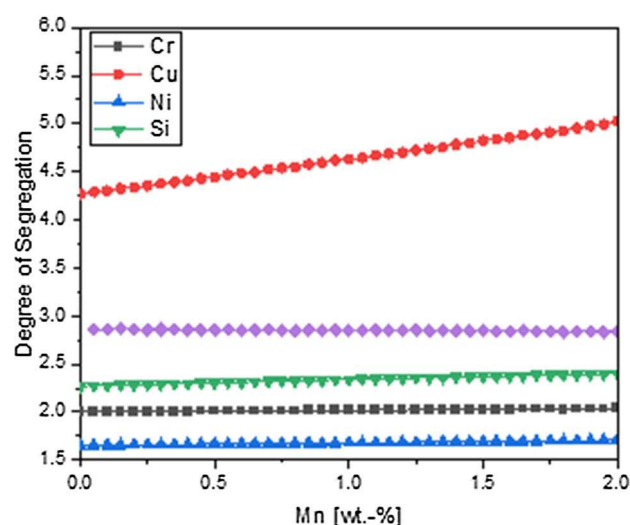


Fig. 2 Exemplary SEM images and qualitative local distributions of alloying elements in (a) 1.4307 and (b) 1.4307_opti

mean values of the M_{d30} temperature and the SFE indicate a higher mean austenite stability of the optimized alloy 1.4307_opti. In contrast, the M_s temperature shows the opposite tendency. M_{d30} of the steel 1.4307_opti is 31.3 °C lower, representing an improvement of 11.2%, while M_s is 73.5 °C higher compared to the steel 1.4307, indicating a 112.8% stability decrease. The divergent trends of M_s and M_{d30} can be mainly attributed to the contribution of the interstitial alloying elements C and N. These elements are considered to have a significantly greater influence on M_s than on M_{d30} (Ref 8, 22,

30). The much higher content of these elements in steel 1.4307 is therefore more evident in M_s than in M_{d30} . This indicates that the M_s temperature might not be suitable for the validation by EDS, which explains the decrease of the mean M_s in the optimized alloy.

As described above, not only the average austenite stability, but also its homogeneity, controls the actual transformation tendency of the austenite, as local stability minima provide favorable sites for martensite formation. For all three parameters describing the austenite stability, the sample standard deviation and mean absolute difference of the aggregated data indicates an improved homogeneity of the austenite stability in the optimized alloy 1.4307_opti. For instance, the expected absolute M_{d30} difference between any two points is 82.9 and 63.5 °C for the reference and optimized alloys, respectively. The relative improvements in terms of the M_s and M_{d30} temperatures are around 20%, while the SFE presents a homogeneity enhancement of 7.4%.

The mean M_{d30} as well as the mean M_s temperature of the steel 1.4307_opti lies well below room temperature and feature improved homogeneities. These factors indicate a reduced tendency to form martensite upon straining at room temperature, compared to the reference steel 1.4307. Moreover, the increased SFE can be considered to contribute to a more homogeneous deformation behavior and the provision of a lower number of nucleation sites for α -martensite due to less ε -martensite (Ref 31). The lower number of nucleation sites for martensite comes through the decreased σ in combination with an increased μ . As pointed out by Noh et al. (Ref 30), a SFE of 20 mJ/m² can be considered as a threshold for the formation of α -martensite. If now more regions in an alloy are locally below a SFE of 20 mJ/m², more nucleations sites for martensites and even more martensite will form. Therefore, the alloy 1.4307_opti can be considered as more resistant against the formation of nucleation sites.

Therefore, the steel 1.4307_opti proves the effectiveness of the implemented optimization approach for the design of a steel with an improved resistance against hydrogen embrittlement, which was the overarching aim. However, future studies have to investigate the mechanical properties of the optimized steel with and without influences of hydrogen. Additionally, some aspects of the optimization procedure are supposed to provide room for further improvement.

3.3 Optimization Strategy

An essential part of this work was the development of a suitable optimization approach. Every optimization approach consists of a fitting analysis model, purposeful objective functions and an appropriate optimization strategy. The optimization is based on the analysis model, in this case the Scheil module. The validity of this model is well documented in the literature and known to be suitable for the calculations that were carried out in the framework of the optimization process (Ref 32, 33). However, the peculiarities of the interstitial elements C and N could not be considered optimally, as these elements could not be defined as “fast diffusing components” because of limitations in the *TC-Python* module, that existed at the time the simulations were performed. The segregation of C and N is therefore assumed to be overestimated in the simulations which, however, could not be proven as these elements cannot be quantified in the EDS measurements.

Besides the analysis model, the optimization depends essentially on the selected objective functions (Ref 34). The objective functions are developed as derivations of stability parameters, which quantify the austenite stability (Ref 8, 22, 23). Consequently, the predictive power of the objective functions depends on the meaningfulness of the stability parameters. Even though considering stability parameters alone is not a sufficient prerequisite for resistance to hydrogen embrittlement, steels with high austenite stability nevertheless exhibit lower susceptibility to hydrogen embrittlement. This renders the approach presented here suitable for the optimization of austenitic steels for the use in hydrogen atmospheres.

The equations of the M_s and M_{d30} temperatures consider a linear influence of the alloying elements on the resulting stability parameter. This disables a consideration of interactions of the alloying elements. Another issue is the allowed alloying range of these stability parameters. King and Larbalestier (Ref 35) restrict the usable range of the M_s temperature, whereas the influence of Cr is considered too high and the influence of Ni is considered too low in the two investigated alloys. This effect is amplified in the higher alloyed regions in the solidification simulations and in the EDS mappings. The M_s temperature should therefore not be used as an exact number, but can be used for a qualitative comparison of the alloy systems.

Both the linear influence and the absence of interactions, as well as the limited alloying range, can be avoided by using the

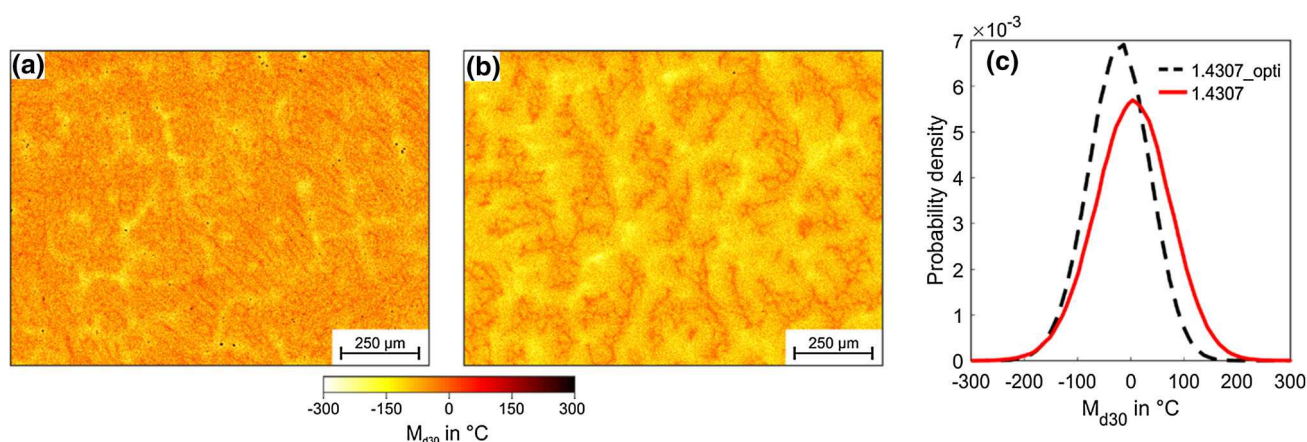


Fig. 3 Local distribution of M_{d30} for (a) 1.4307 and (b) 1.4307_opti calculated from quantified EDS datasets shown in Fig. 3. (c) shows the frequency distributions of M_{d30} in (a) and (b)

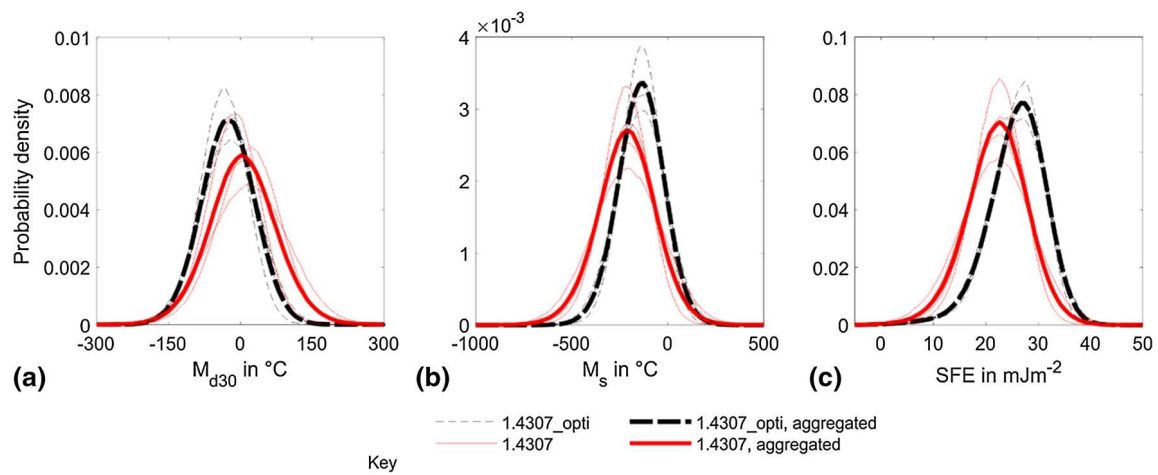


Fig. 4 Histograms of (a) M_{d30} , (b) M_s and (c) SFE. The fine lines represent the individual distributions of each measured field (1–4 for each alloy), while the broad lines correspond to their aggregation

Table 3 Parameters μ and σ of normal distributions fitted to datasets of M_s , M_{d30} , SFE calculated from EDS data

Dataset	M_{d30} [°C]			M_s [°C]			SFE [mJm ⁻²]		
	μ	σ	MAD	μ	σ	MAD	μ	σ	MAD
1.4307 #1	16.7	82.9	93.2	– 212.3	186.3	209.4	21.8	7.1	7.9
1.4307 #2	3.4	71.1	79.9	– 213.1	159.7	179.0	21.9	6.2	6.9
1.4307 #3	– 14.5	55.9	62.4	– 219.6	124.7	138.9	22.2	4.9	5.4
1.4307 #4	16.7	66.2	74.0	– 208.2	146.5	163.1	22.4	5.7	6.3
1.4307 #1–4	5.6	70.8	79.2	– 213.3	156.0	173.6	22.1	6.0	6.7
1.4307_opti #1	– 34.8	48.9	55.0	– 139.3	104.0	116.9	25.8	5.2	5.7
1.4307_opti #2	– 23.1	55.0	61.99	– 141.3	118.4	113.3	25.9	5.4	6.0
1.4307_opti #3	– 22.6	61.8	69.7	– 140.2	133.7	150.7	25.8	5.9	6.5
1.4307_opti #4	– 22.5	58.0	65.4	– 138.3	125.1	140.9	26.1	6.0	6.5
1.4307_opti #1–4	– 25.7	56.4	63.5	– 139.8	120.8	135.7	25.9	5.6	6.2
Rel. improvement in %	11.2	20.5	19.9	– 122.8	22.5	21.8	17.2	6.2	7.4

High importance values are given in bold

SFE formula (Ref 23). However, when using the empirical formula to calculate the SFE, attention must be paid to nonlinearity, since the minima and maxima of the function do not necessarily have exist in the areas that solidified first or last.

Overall, it must also be considered that the austenite stability was also determined for ferritic bcc phase solidifying from the melt. Since it is actually physically incorrect to calculate M_s and M_{d30} for ferrite, the usage of a Ni-equivalent might be a better alternative (Ref 36). On the other hand, especially the M_{d30} is well known for its significant correlation with the resistance against hydrogen environment embrittlement, which makes M_{d30} a meaningful parameter in the context of this study (Ref 2, 3, 14).

The method of distance functions was used as the optimization strategy in this study, as each objective function was supposed to be considered equally. Also, the method was normalized by relative distances with the weights not being predefined, but a result from the values of the objective functions. This is contrasted with the fact that the method of restriction-oriented transformation is considered the best method for Pareto optimization (Ref 34). This method is based on the formulation of a main objective and secondary objectives. Secondary objectives are seen only as constraints

that define the limits of the optimization. The formulation of a single main objective function is not possible in this case, because all objective functions, and stability parameters, respectively, represent an important parameter and point to different aspects of the phase transformation and therefore HEE. In particular, the quality of the stability parameters and thus of the functions is difficult to evaluate, which is why this method should not be used here. As the here used optimization strategy is independent of a single objective function, it is considered more suitable for the described application (Ref 25).

The considered optimization scheme has the goal to achieve a homogeneous and sufficient stable primary microstructure regarding the empirical formulations. Nevertheless, the secondary microstructure determines the characteristics and properties of a material or alloy, respectively. The secondary microstructure is determined by the primary microstructure due to the casting process and the secondary manufacturing processes like rolling or casting. Therefore, the primary microstructure plays a significant role for the secondary microstructure (Ref 37). If the secondary process is now considered as equal for both the optimized and conventional 1.4307, the optimized alloy will again show improved homogeneity regarding the stability parameters considered.

4. Summary

In this work, a novel approach for the optimization of austenitic stainless steel was implemented and validated. The presented approach incorporates an automated optimization strategy, which targets material properties, that are strongly influenced by segregation effects of the alloying elements. The following conclusions can be drawn from the investigations:

- By coupling Scheil–Gulliver solidification simulations with optimization functions, the chemical composition can be optimized to improve the overall austenite stability.
- Empirical equations describing the austenite stability are suited to serve as objective functions for multi-objective optimization strategies.
- The conceived optimization approach was successfully used to achieve an improved austenite stability within the alloying range of the steel 1.4307, which was proved by assessing local austenite stability distributions in laboratory-scale ingots.

In future attempts to develop novel alloys with optimized properties, the presented approach can be used beyond standardized compositional ranges, by shifting boundary conditions and adding more elements. By employing different objective functions, the approach can also be adapted to pursue the optimization of other material properties, e.g., corrosion resistance, or a combination of different properties. Upcoming studies will also investigate the here presented alloy 1.4307_opti in tensile tests in air and H₂-atmosphere. These tests will prove the improved properties of the optimized alloy and will validate the optimization procedure.

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