Doctoral Thesis

Fe–Mn–Pd maraging steels for biodegradable implant applications

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Fe–Mn–Pd maraging steels for biodegradable implant applications

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(Dr. sc. ETH Zurich)

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2014
“The finest steel has to go through the hottest fire”

(John N. Mitchell)
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Contents

Abstract ix
Zusammenfassung xi

1 Introduction 1
  1.1 General remarks 2
  1.2 Biodegradable metals 3
    1.2.1 Concept 3
    1.2.2 Recent developments of biodegradable Fe-based alloys 5
    1.2.3 Degradation behavior of Fe and Fe-based alloys in physiological media 8
    1.2.4 Biocompatibility considerations regarding Fe and Fe–Mn–Pd alloys 11
  1.3 Fe–Mn-based alloys 13
    1.3.1 Phase transformations in the Fe–Mn system 13
    1.3.2 Microstructure and mechanical behavior of Fe–Mn alloys with lath martensite 15
    1.3.3 Fe–Mn-based maraging steels 18
  1.4 Atom probe tomography 22
  1.5 Aim and outline of the thesis 26
References 27

2. Precipitation hardening 35
Precipitation hardening of biodegradable Fe–Mn–Pd alloys
  2.1 Introduction 36
  2.2 Experimental section 38
  2.3 Results 39
    2.3.1 Hardness measurements 39
    2.3.2 Microstructural analysis 40
      2.3.2.1 Transmission electron microscopy observations 40
2.3.2.2 Three-dimensional atom probe measurements ........................................... 45
2.3.2.3 XRD measurements .................................................................................. 48

2.4 Discussion ............................................................................................................. 49
  2.4.1 Strengthening behavior .................................................................................. 49
  2.4.2 Microstructure .............................................................................................. 51

2.5 Summary and conclusion ..................................................................................... 53

References ................................................................................................................... 54

3. Precipitation sequence ............................................................................................ 57

3.1 Introduction ........................................................................................................... 58

3.2 Experimental procedure ...................................................................................... 60

3.3 Results and discussion ....................................................................................... 61
  3.3.1 Mechanical properties .................................................................................. 61
  3.3.2 Optical microscopy ...................................................................................... 62
  3.3.3 Atom probe tomography ............................................................................. 67
  3.3.4 X-ray diffraction .......................................................................................... 66

3.4 Summary .............................................................................................................. 70

References ................................................................................................................... 70

4. Overall transformations processes ........................................................................... 73

4.1 Introduction .......................................................................................................... 74

4.2 Experimental procedure ...................................................................................... 76

4.3 Thermo-kinetic simulation .................................................................................. 77

4.4 Results .................................................................................................................. 78
  4.4.1 Isothermal aging .......................................................................................... 78
  4.4.2 Continuous heating dilatometry ................................................................... 79
  4.4.3 Thermo-kinetic simulations .......................................................................... 81
4.4.4 Atom probe tomography ........................................ 83
4.5 Discussion ................................................................... 85
  4.5.1 Precipitation reaction ............................................. 85
  4.5.2 Reverse $\alpha' \rightarrow \gamma$ transformation ......................... 86
    4.5.2.1 Reverse $\alpha' \rightarrow \gamma$ transformation on fast heating (200 K/min) .......... 86
    4.5.2.2 Reverse $\alpha' \rightarrow \gamma$ transformation on slow heating (0.5 K/min) .......... 90
4.6 Conclusions .................................................................. 93
References ......................................................................... 94

5 Mechanical performance .................................................. 97
Atomic-scale characterization of prior austenite grain boundaries in Fe–Mn-based maraging steel using site-specific atom-probe tomography

  5.1 Introduction .................................................................. 98
  5.2 Experimental procedure .............................................. 100
  5.3 Results ........................................................................ 102
    5.3.1 Mechanical tests ................................................... 102
    5.3.2 X-ray diffraction ................................................... 104
    5.3.3 Atom probe tomography ......................................... 105
      5.3.3.1 Fe-10Mn-1Pd peak-aged condition (30min/500°C) ......................... 105
      5.3.3.2 Fe-10Mn-1Pd over-aged condition (30h/500°C) ......................... 107
  5.4 Discussion .................................................................. 109
    5.4.1 Fe-10Mn ............................................................... 109
    5.4.2 Fe-10Mn-1Pd ........................................................ 110
      5.4.2.1 Mn segregation as source of embrittlement ......................... 110
      5.4.2.2 Precipitates as source of embrittlement ......................... 115
  5.5 Summary and conclusions .......................................... 117
References ......................................................................... 118
6 In-vivo degradation performance .................................................................123
Biodegradable Fe-based alloys for use in osteosynthesis – outcome of an
in-vivo study after 52 weeks

6.1 Introduction .................................................................................................124

6.2 Materials and methods ...............................................................................126
  6.2.1 Implants .................................................................................................126
  6.2.2 Experimental design ...............................................................................127
  6.2.3 Surgical procedure and postoperative treatment ...................................127
  6.2.4 Euthanasia .............................................................................................127
  6.2.5 Preparation of the bone-pin model .......................................................127
  6.2.6 High-resolution microfocus computed tomography and image
      reconstruction ..........................................................................................128
  6.2.7 Determination of weight loss after explantation ....................................128
  6.2.8 Surface analysis ....................................................................................128
  6.2.9 Histological processing .........................................................................129
  6.2.10 Statistics ..............................................................................................129

6.3 Results .........................................................................................................130
  6.3.1 Clinical findings ....................................................................................130
  6.3.2 Determination of the in-vivo degradation .............................................130
  6.3.3 Surface analysis ....................................................................................131
  6.3.4 Iron accumulation around the implants ................................................134

6.4 Discussion ....................................................................................................135
  6.4.1 Determination of the degradation rate ..................................................135
  6.4.2 Factors that influence the degradation of Fe-based materials ..............136
  6.4.3 Iron release to the surrounding tissue ..................................................138
  6.4.4 Implications for future material development ........................................139

6.5 Summary ......................................................................................................139

References ........................................................................................................140
# Summary and outlook

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Summary</td>
<td>144</td>
</tr>
<tr>
<td>7.2 Outlook</td>
<td>146</td>
</tr>
</tbody>
</table>

# Appendix

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curriculum vitae</td>
<td>150</td>
</tr>
</tbody>
</table>
Abstract

Metallic implants are commonly known for their high corrosion resistance. However, there are a number of clinical applications where patients may benefit from a metallic material which degrades after the healing process is complete. Iron (Fe) and in particular Fe-based alloys feature an attractive combination of mechanical, electrochemical and biological properties, and are thus considered as promising candidates. In preliminary animal (in-vivo) studies the potential of pure Fe as biodegradable implant material has been demonstrated. However, it has been noted that Fe exhibits a too slow in-vivo degradation rate.

In the course of this thesis, a new class of high-strength biodegradable Fe-based steels (Fe–Mn–Pd) has been developed. The occurring phase transformations, related microstructural and property changes as well as the biological performance have been throughout investigated. The material development is based on a design strategy, which includes the following three aspects: (i) addition of manganese (Mn, less noble than Fe) to reduce the standard electrode potential of the matrix and to consequently increase the corrosion susceptibility; (ii) addition of minor amounts of palladium (Pd, more noble than Fe) to generate noble finely dispersed intermetallic particles; these act as cathodic sites and induce microgalvanic corrosion; and (iii) development of high-strength alloys, in order to reduce implant dimensions so that less material needs to degrade. Previous works confirmed the feasibility of the alloying strategy. Fe-based alloys containing Mn and/or Pd exhibited suitable biocompatibility and a significant increased degradation rate in laboratory tests (in-vitro) compared to pure Fe.

In this thesis a main focus is the development of a high-strength material. Fe-based alloys containing 5 and 10 wt.% Mn with and without the addition of 1 to 6 wt.% Pd were investigated. These alloys exhibit a characteristic lath martensitic (α′-martensite) structure in the initial state. The Pd-containing specimens revealed a very interesting hardening behavior after isothermal heat treatment (aging) in the two-phase field ferrite (α) and austenite (γ). In comparison to binary steels, aging the ternary Fe–Mn–Pd alloys produced a drastic increase in hardness (nearly 300% greater hardness for Fe-10Mn-6Pd in the peak-aged condition than for Fe-10Mn in the initial state). By means of transmission electron microscopy (TEM) and atom probe tomography (APT) investigations this pronounced strengthening was associated with the formation of nanometer-sized precipitates rich in Pd and Mn which formed within
the $\alpha'$-martensite matrix. The age-hardening behavior is similar to that of maraging steels, and accordingly the martensitic Fe–Mn–Pd alloys can be assigned to this steel family. The structure and chemical composition of the hardening phase was analyzed. It was observed that the precipitation sequence proceeds similar to that of Fe–Mn–Ni and Fe–Mn–Pt maraging steels.

In addition to precipitation formation, austenite evolves during isothermal aging ($\alpha'\rightarrow\gamma$). Both reactions play a major role in maraging steels, as they significantly affect their mechanical properties. In this context the mechanisms governing the reverse $\alpha'\rightarrow\gamma$ transformation for binary Fe–Mn steels and the effect of prior precipitation on austenite reversion was studied with regard to ternary Fe–Mn–Pd alloys. Through a combination of dilatometry and thermo-kinetic solid-state simulation, a consistent picture was elaborated of the process which occurs during fast and slow continuous heating.

The mechanical properties of binary Fe–Mn (Fe-10Mn) and ternary Fe–Mn–Pd (Fe-10Mn-1Pd) alloys were determined as a function of aging time at 500 °C. For Fe-10Mn a decrease in strength with a considerable increase in uniform elongation was observed. In contrast, in the ternary counterpart a ductile-brittle-ductile transition upon aging was noted. The embrittlement occurred in the under- and peak-aged regimes. It was characterized by intergranular fracture along prior austenite grain boundaries (PAGBs) and by failure of the elastic regime in tensile tests. In the over-aged state tensile ductility recovered, and Fe-10Mn-1Pd still possessed high strength. Site-specific APT investigations of PAGBs were performed to study microstructural changes after aging. The microstructural features observed were correlated with the mechanical properties measured. Various embrittlement and de-embrittlement mechanisms were proposed and discussed with regard to the existing literature.

An animal study was performed to assess the biological performance of these novel high-strength alloys. Pins of pure Fe, Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd were implanted into the femurs (thigh bones) of rats. The *in-vivo* study was performed over a period of 52 weeks. The materials investigated showed signs of degradation. However, the *in-vivo* degradation rate was unexpectedly slow, and no difference between pure Fe and the Pd-containing alloys was apparent. Fundamental aspects of the *in-vivo* degradation were also considered and discussed.
Zusammenfassung


Im Zuge dieser Arbeit wurde eine neue Klasse von hochfesten biodegradierbaren Fe-basierten Legierungen (Fe–Mn–Pd) entwickelt. Die auftretenden Phasentransformationen, die damit verbundenen Mikrostruktur- und Eigenschaftsänderungen sowie das biologische Verhalten wurden untersucht. Die Werkstoffentwicklung basiert dabei auf einer Legierungsstrategie, welche die folgenden drei Aspekte beinhaltet: (i) die Zugabe von Mangan (Mn, unedler als Fe), um das Standardelektrodenpotential der Matrix zu reduzieren, so dass sich die Korrosionsanfälligkeit erhöht; (ii) die Zugabe von geringen Mengen von Palladium (Pd, edler als Fe), um edle feinverteilte intermetallische Partikel zu erzeugen, welche als kathodische Elemente wirken und mikrogalvanische Korrosion verursachen; (iii) die Entwicklung einer hochfesten Legierung, um Implantatabmessungen zu reduzieren, so dass weniger Material degradieren muss. In vorangehenden Arbeiten wurde die Durchführbarkeit der Legierungsstrategie aufgezeigt. Fe-basierte Legierungen die Mn und/oder Pd beinhalten zeigten eine geeignete Biokompatibilität und eine signifikant erhöhte Degradationsrate in Labortests (in-vitro) im Vergleich zu Fe.

In der vorliegenden Arbeit wurde das Hauptaugenmerk vor allem auf die Entwicklung eines hochfesten Werkstoffes gelegt. Legierungen mit 5 und 10 Gew.-% Mn mit und ohne Zusätzen von 1 bis 6 Gew.-% Pd wurden untersucht. Diese Legierungen besitzen im Ausgangszustand eine charakteristische Lattenmartensitstruktur (α'-Martensit). Die Pd-haltigen Proben zeigten nach isothermer Wärmebehandlung (Auszügung) im Zweiphasengebiet Ferrit (α) und Austenit (γ) ein sehr interessantes Aushärteverhalten. Im Vergleich zu den binären Stählen führte die Auszügung bei den ternären Fe–Mn–Pd Legierungen zu einem
drastischen Anstieg in der Härte (fast 300% höhere Festigkeit von Fe-10Mn-6Pd im maximal ausgehärteten Zustand im Vergleich zu Fe-10Mn im Ausgangszustand). Mittels Transmissionselektronenmikroskopie (TEM) und Atomsondeuntersuchungen (APT) konnte die ausgeprägte Festigkeitssteigerung auf die Bildung von Pd und Mn angereicherten, Nanometer-grossen Ausscheidungen zurückgeführt werden, die sich in der α'-Martensit Matrix gebildet haben. Das Aushärteverhalten ist ähnlich dem von Maraging-Stählen und entsprechend können die martensitschen Fe–Mn–Pd Legierungen dieser Stahlfamilie zugeordnet werden. Die Struktur und die chemische Zusammensetzung der Aushärtephase wurde analysiert. Es wurde beobachtet, dass die Ausscheidungssequenz ähnlich wie in Fe–Mn–Ni und Fe–Mn–Pt Maraging-Stählen verläuft.

Neben der Ausscheidungsbildung entsteht während der isothermen Auslagerung auch Austenit (α'→γ). Beide Reaktionen spielen eine wichtige Rolle in Maraging-Stählen, da sie die mechanischen Eigenschaften massgeblich beeinflussen. In diesem Zusammenhang wurden die Mechanismen, welche die α'→γ Transformation bestimmen, für binäre Fe–Mn Stähle und der Effekt von zuvor stattfindender Ausscheidungsbildung auf die Austenit-Rückumwandlung für ternäre Fe–Mn–Pd Legierungen untersucht. Durch die Kombination von Dilatometrie und thermokinetischen Festkörpersimulationen wurde ein konsistentes Bild der Prozesse erarbeitet, die bei schneller und langsamer kontinuierlicher Aufheizung auftreten.

Die mechanischen Eigenschaften von binären Fe–Mn (Fe-10Mn) und ternären Fe–Mn–Pd (Fe-10Mn-1Pd) Legierungen wurden als Funktion der Auslagerungszeit bei 500 °C bestimmt. Für Fe-10Mn wurde eine Erniedrigung der Festigkeit zusammen mit einer beträchtlichen Zunahme der Gleichmassdehnung beobachtet. Im Gegensatz dazu wurde für Fe-10Mn-1Pd ein duktil-spröd-duktil Übergang während der Auslagerung festgestellt. Die Versprödung trat im unteralterten Bereich und in der Region der maximalen Härte auf. Sie ist charakterisiert durch intergranularen Bruch entlang der ehemaligen Austenitkorngrenzen (PAGBs) und durch Versagen im elastischen Bereich in Zugversuchen. Im überalterten-Bereich kam es zu einer beträchtlichen Erholung der Zug-Duktilität, wobei Fe-10Mn-1Pd weiterhin eine hohe Feistigkeit aufwies. Ortsspezifische Atomsondeuntersuchungen von PAGBs wurden durchgeführt, um deren mikrostruturellen Änderungen nach Auslagerung zu untersuchen. Die beobachteten mikrostruturellen Merkmale wurden mit den gemessen mechanischen
1 Introduction

The following aspects are addressed in this introduction: (i) general considerations of phase transformations in steels and their importance for alloy development; (ii) concepts of biodegradable metals and recent developments covering specifically biodegradable Fe-based alloys; (iii) the Fe–Mn system and its phase transformations, with a focus on Fe–Mn-based maraging systems; (iv) basics of atom probe tomography and (v) the aim and outline of this thesis.
1.1 General remarks

Fe-based alloys have a long history in the field of medical applications and the austenitic stainless steel grade 316L is still one of the most widely used implant materials. As outlined in the strategic report “Metallurgy Europe – A Renaissance Program for 2012-2022” [1] future requirements for metals include among other things “better biocompatibility and/or resorbability for medical applications”. In this context Fe or Fe-based alloys are considered to be promising materials for temporary implant applications [2]. Preliminary animal studies conducted with pure Fe have demonstrated its potential for application as biodegradable implant material, but have also revealed its main drawback: Fe has a rather low in-vivo degradation rate [3-5]. In our group, however, novel biodegradable Fe–Mn-based steels with minor additions of Pd have been developed [6]. These alloys show promising results in terms of increased in-vitro degradation rates in physiological media, in combination with improved mechanical properties. The design strategy underlying these novel biodegradable Fe–Mn–Pd alloys is described in detail in section 1.2 below.

In addition to applications as temporary implant material, Fe–Mn-based steels have attracted great interest in the field of high strength steels [7-9]. The Fe–Mn system is very interesting because it exhibits a wide variety of phase transformations. Binary Fe–Mn alloys (<28 wt.% Mn) exhibit martensitic phase transformation upon cooling from the austenite phase field [10], thereby developing a complex microstructure consisting of austenite, α’-martensite and/or ε-martensite domains. By varying the Mn content and temperature, various deformation modes (slip, twinning, strain-induced phase transformations) can occur in these alloys [11, 12]. The exceptional variety of mechanical properties can be further adjusted by adding alloying elements to induce either TRIP-type (Transformation Induced Plasticity) [13], TWIP-type (Twinning Induced Plasticity) [14], shape memory effect [15] or maraging-type behavior [16]. Hence understanding phase transformation, the associated microstructural changes, and the related property changes is crucial in the development of new steels. In this thesis Fe–Mn alloys containing 5-10 wt.% Mn with additions of Pd (1-6 wt.%) have been investigated. Upon quenching from elevated temperatures to room temperature, these alloys exhibit a microstructure typical of maraging steels. Section 1.3 below provides an overview of the Fe–Mn system in this regard, with a special focus on Fe–Mn-based maraging steels.
In modern steel research there is a growing interest in nano-engineering. Novel steels such as nano structured bainite have been developed, and are already commercially available in huge quantities [17]. Exploring nano structured steels requires characterization via multiple techniques. Besides transmission electron microscopy (TEM) and X-ray (XRD) or neutron diffraction, methods which are already well established and have constantly matured over the years, atom probe tomography (APT) is experiencing a renaissance. This is promoted by the development of commercially available instruments that are reliable and allow detection of hundreds of millions of atoms in reasonable time periods. New innovations in pulsed laser APT, which enables the nm-scale characterization of non-metallic materials [18], are also significant. APT measurements were performed throughout the thesis work; section 1.4 below therefore describes the basics of APT.

1.2 Biodegradable metals

1.2.1 Concept

Metals are applied widely in medicine, mainly because of their excellent combination of strength, stiffness and ductility, which is superior to that of polymers or ceramics in areas subjected to high mechanical loads. As implant material they are mainly employed for two applications: (i) prostheses such as hip-, knee- and shoulder-joints; and (ii) fixation of structures such as screws, plates, wires, intramedullary nails and stents [19]. Classical implant materials such as stainless steels, cobalt–chromium-based alloys and titanium-based alloys were designed to remain in the patient for a long time. Apart from the appropriate mechanical properties such as strength, stiffness, wear resistance and fatigue properties, a high corrosion resistance in physiological media is a target for these metals. The high corrosion resistance relies on the formation of a passivating metal-oxide film on the metal surface, which persists in the body and inhibits metal dissolution. In stainless steels high corrosion resistance is achieved by adding at least 10.5 % chromium, which generates a protective chromium-oxide surface film (~3 nm thick) [20].

However, even though permanent metal implants have been successfully deployed over the last few decades they have certain disadvantages. In many osteosynthesis applications the implant needs to be removed after one or two years. The patient has to undergo the pain of a second surgery and accept risks such as refracture, neurovascular injuries or even implant failure. From an economic point of view this also means considerable costs also for health
care systems -- and implant removal accounts for up to 30% of orthopedic procedures [21]. Stainless steel or Co–Cr alloys contain allergens such as nickel, chromium or cobalt. Although these alloys possess high corrosion resistance, wear or unfavorable conditions in the area of metal-to-metal contact (e.g. screw heads on plates) can increase the release of metal ions. This may stimulate sensitivity to the various metal components or allergic reactions, e.g. localized eczema near the implant site [22]. A prominent current example of permanent implant application is the coronary stent. This field (the first attempts were conducted in 1986 by Sigwart, Puel and others [23]) is booming. Stents are metallic wire meshes which by means of a balloon catheter are introduced into narrowed arteries to keep the lumen open. Although stents are successfully and widely deployed they do have some risks. Bare metal stents are associated with a 20-30% restenosis1 rate, which requires reintervention (i.e. re-stenting) [24]. Drug-eluting stents were developed to minimize the risk of restenosis. However, there are indications that these stents present a higher risk of late thrombosis2, which can lead to a heart attack or sometimes death [25]. It has also been

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1Restenosis = narrowing of blood vessels;
2Thrombosis = formation of blood clot, which can hamper the normal blood flow;
3hallux valgus = “hallux” means great toe and “valgus” refers to abnormal angulation
observed that remodeling of the vessel occurs within a period of 6-12 months, meaning that after that period the supporting function of the stent is actually no longer required [30, 31]. For these reasons, in a number of clinical applications a metal that degrades when no longer needed would be highly desirable to circumvent the disadvantages of permanent implant materials. This basically simple idea of degradable metals, however, represents an opposing concept in the implant development compared to the classical materials where inertness and high corrosion resistance was aimed at. Ideally biodegradable metals should feature a tradeoff between mechanical integrity and degradation. The temporary support should be maintained until healing is completed and hence the degradation progress must be tailored such that mechanical integrity does not deteriorate too fast (Fig. 1.1A). In addition, the degradation progress may not cause any accumulation of degradation products around the implant or in systemic organs, and degradation products may not produce any adverse effects. In these respects it is obvious that biodegradable metals can only be used in small, lightweight implants. Accordingly, research has mainly focused on the development of degradable stents or small screws or plates for osteosynthesis. Fig. 1.1 gives an overview of selected examples.

1.2.2 Recent developments of biodegradable Fe-based alloys

In the field of biodegradable metals mainly Fe and Mg and their alloys have been investigated, in a number of in-vitro and in-vivo studies [27, 32]. Both iron and magnesium are essential elements in the human body; adult men normally contain 35 to 45 mg of Fe per kilogram body weight [33] and 21 to 28 g of Mg [34]. Mg-based alloys are well established as material for temporary implant applications, and have already undergone human clinical trials in the field of osteosynthesis [28] and in particular stent applications [35-37]. However, Mg-based alloys are known to exhibit too-rapid degradation rates in physiological environments. In addition, during the degradation process hydrogen may evolve. This can generate gas cavities at the implantation side which can be problematic, for example for bone healing [38]. Although Mg-based alloys have been developed which have acceptable strength and ductility values, materials with better mechanical performance would also be highly desirable. In this respect Fe and in particular its alloys have been proposed as a promising alternative [27, 32]. Fe-based alloys possess superior mechanical properties compared to Mg, enabling versatile implant design and fabrication of filigree structures.
Compared to Mg, Fe is also radio-opaque, which in stents facilitates placement via coronary angioplasty. The main drawback of Fe in contrast to Mg, however, is its rather slow degradation rate in physiological media [27, 32].

In literature various approaches have been described to increase the degradation rate of Fe. They basically involve (i) alloying and (ii) special fabrication methods. Table 1.1 gives an overview of the various strategies proposed. First Hermawan et al. [39] and later

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Approach/Aim</th>
<th>Ref. (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Mn</td>
<td>Alloying via powder-metallurgy</td>
<td>Addition of Mn within solubility limit of Fe, to reduce standard electrode potential of Fe–Mn alloys compared to pure Fe.</td>
<td>[39] (Hermawan et al. 2007)</td>
</tr>
<tr>
<td>Fe–Mn–Pd</td>
<td>Alloying + heat treatments</td>
<td>Addition of Mn to reduce standard potential and minor addition of Pd to form noble precipitates to induce microgalvanic corrosion. Improved strength via heat treatments to reduce implant dimensions</td>
<td>[6] (Schinhammer et al. 2010)</td>
</tr>
<tr>
<td>Fe</td>
<td>Electroforming of Fe sheets</td>
<td>Evaluation to increase degradation rate of Fe via electroforming</td>
<td>[40] (Moravej et al. 2010)</td>
</tr>
<tr>
<td>Fe</td>
<td>Severe plastic deformation (via ECAP)</td>
<td>Study corrosion rate and enhance biocompatibility through nanocrystalline Fe produced by ECAP.</td>
<td>[41] (Nie et al. 2010)</td>
</tr>
<tr>
<td>Fe–Mn–Si</td>
<td>Alloying</td>
<td>Evaluation of an iron-based shape memory alloy as degradable biomaterial</td>
<td>[42] (Liu et al. 2011)</td>
</tr>
<tr>
<td>Fe–X (X= Mn, Co, Al, W, Sn, B, C, S)</td>
<td>Alloying</td>
<td>Feasibility of different binary Fe alloys for use as degradable biomaterial</td>
<td>[43] (Liu et al. 2011)</td>
</tr>
<tr>
<td>Fe–X (X= P, B, Ag)</td>
<td>Alloying via powder-metallurgy</td>
<td>Development of a degradable Fe-based alloy with the idea of using them as matrix material of cellular structures producible via powder metallurgy</td>
<td>[44] (Wegener et al. 2011)</td>
</tr>
<tr>
<td>Fe–N</td>
<td>Alloying via vacuum plasma nitriding of Fe</td>
<td>Improve strength via nitriding to reduce implant dimension; formation of Fe/N-particles to induce galvanic corrosion</td>
<td>[45] (Feng et al. 2013)</td>
</tr>
<tr>
<td>Fe–X composites (X=W, CNT**)</td>
<td>Spark plasma sintering</td>
<td>Improve strength and induce galvanic corrosion through the incorporation of the X-Phase</td>
<td>[46] (Cheng et al. 2013)</td>
</tr>
<tr>
<td>Fe–Pd, Fe–Pt</td>
<td>Alloying via spark plasma sintering</td>
<td>Acceleration of degradation rate through the addition of Pd or Pt</td>
<td>[47] (Huang et al. 2014)</td>
</tr>
</tbody>
</table>

Table 1.1. Overview of various strategies for developing a biodegradable Fe-based alloy.

1ECAP... Equal channel angular pressure
2CNT... nonmetal carbon nanotube
Schinhammer et al. [6] developed pioneering concepts regarding alloying strategies. Hermawan et al. [39], based on metallurgical and toxicological considerations, introduced the adding of Mn, within the solubility limit of Fe, to achieve higher degradation rates. Mn exhibits a lower standard electrode potential (Fig. 1.2b) than Fe. Consequently binary Fe–Mn becomes less noble, exhibiting a greater corrosion susceptibility than Fe. This concept was extended and advanced in our group by Schinhammer et al. [6], leading to the development of Fe–Mn–Pd alloys. Their approach incorporates two further aspects (Fig. 1.2a). First, to further enhance the degradation rate minor amounts of Pd were added to generate, by appropriate heat treatments, noble finely dispersed Pd-rich intermetallic precipitates, which act as cathodic sites and induce microgalvanic corrosion. Second, an alloy exhibiting high strength is the aim. This is important because smaller implant dimensions thereby become feasible and thus less material has to degrade. Fig. 1.2a again summarizes the ideas behind the design strategy, which this thesis has used as a guideline with a special focus on the development of high-strength alloys.

![Fig. 1.2 (a) Design strategy for the Fe–Mn–Pd alloys. (b) Electromotive force series [20].](image)

In later studies, basically no fundamentally new aspects regarding alloying strategies were elaborated. Liu et al. [42] investigated an Fe–Mn–Si alloy, which is a promising shape memory alloy for pipe joints. In a later work, Liu et al. [43] screened various binary Fe–X alloys (X = Mn, Co, Al, W, Sn, B, and C) regarding biodegradability and biocompatibility. Their choice of alloying elements was based on the consideration that most are well-known additives to steels and some may generate an increase in degradation rate. Wegener et al. [44] investigated binary Fe–X (X= P, B, Ag) alloys using a powder-metallurgical fabrication route. B and P were chosen as they can increase the sintering density. Ag was selected
because Ag and Fe are not soluble and Ag-particles were expected to act as local galvanic corrosion spots. Feng et al. [45] used plasma nitriding to improve the strength of Fe and thus to decrease implant dimension. They also expected that fine dispersed particles of Fe and N could induce microgalvanic corrosion. Cheng et al. [46] also designed composites Fe–X (X=W, CNT) with the idea of incorporating the X-Phase to simultaneously reinforce Fe and induce microgalvanic corrosion. Recently Huang et al. [47] investigated Fe-5Pd and Fe-5Pt alloys produced via spark plasma sintering. They observed that the materials investigated exhibit a greatly increased degradation rate and improved mechanical properties compared to Fe. Besides these efforts, special fabrication methods such as electroforming [40] and severe plastic deformation [41] have been investigated with the aim of increasing the degradation rate of Fe.

### 1.2.3 Degradation behavior of Fe and Fe-based alloys in physiological media

When a metal is implanted it comes into contact with soft or hard tissue and is continuously exposed to corrosive body fluid, which among other things contains dissolved oxygen, sodium chloride, phosphate, carbonates, calcium, other salts, and complex organic compounds such as proteins. In order to mimic in-vivo conditions in laboratory tests, simulated physiological media are used, such as Hank’s solution (HS), simulated body fluid (SBF), and phosphate-buffered saline (PBS). Degradation behavior is typically investigated by means of immersion tests, where mass loss or dissolved ion concentrations as a function of immersion time are measured to evaluate degradation rates. Electrochemical methods including potentiodynamic polarization measurements and impedance spectroscopy are also often utilized to determine degradation rates. These methods also allow characterization of the corrosion process involved. Table 1.2 summarizes the degradation rates of Fe and various Fe-based alloys which were introduced in the previous sections. Compared to the data for Fe, big discrepancies are apparent. These may relate to differences in the measurement conditions employed, such as the test media (HS, SBF or PBS), buffering system, test method (immersion or potentiodynamic polarization), dynamic or static test conditions, and the time periods investigated. However, despite the lack of comparability between the different investigations it is clear that alloys containing Mn and/or Pd exhibit an increased in in-vitro degradation rate compared to Fe.
Table 1.2. Comparison of the in-vitro degradation rates of Fe and various Fe-based alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Test medium</th>
<th>Test method</th>
<th>Degradation rate</th>
<th>Converted (mm/year)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>HS</td>
<td>PD</td>
<td>16 µA/cm²</td>
<td>0.2</td>
<td>[48]</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>HS</td>
<td>PD</td>
<td>40-91 µA/cm²</td>
<td>0.5-1.1</td>
<td>(Hermawan et al. 2010)</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>HS</td>
<td>PD</td>
<td>37-55 µA/cm²</td>
<td>0.4-0.7</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>SBF</td>
<td>IM</td>
<td>0.0026 mg/(cm²h)</td>
<td>0.03</td>
<td>[6]</td>
</tr>
<tr>
<td>Fe-10Mn</td>
<td>SBF</td>
<td>IM</td>
<td>0.011 mg/(cm²h)</td>
<td>0.12</td>
<td>(Schinhammer et al. 2010)</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>SBF</td>
<td>IM</td>
<td>0.038 mg/(cm²h)</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>HS</td>
<td>PD</td>
<td>8.96 µA/cm²</td>
<td>0.1</td>
<td>[42]</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>HS</td>
<td>PD</td>
<td>10.7 µA/cm²</td>
<td>0.12</td>
<td>(Liu et al. 2011)</td>
</tr>
<tr>
<td>Fe-30Mn-6Si</td>
<td>HS</td>
<td>PD</td>
<td>24.7 µA/cm²</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>PBS</td>
<td>PD</td>
<td>10.887 µA/cm²</td>
<td>0.13</td>
<td>[45]</td>
</tr>
<tr>
<td>Fe-N</td>
<td>PBS</td>
<td>PD</td>
<td>19.365 µA/cm²</td>
<td>0.22</td>
<td>(Feng et al. 2013)</td>
</tr>
<tr>
<td>Fe</td>
<td>HS</td>
<td>PD</td>
<td>0.652 µA/cm²</td>
<td>0.01</td>
<td>[46]</td>
</tr>
<tr>
<td>Fe-2W</td>
<td>HS</td>
<td>PD</td>
<td>6.392 µA/cm²</td>
<td>0.07</td>
<td>(Cheng et al. 2013)</td>
</tr>
<tr>
<td>Fe-0.5CNT</td>
<td>HS</td>
<td>PD</td>
<td>8.397 µA/cm²</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>HS</td>
<td>IM</td>
<td>0.044 mg/(cm²d)</td>
<td>0.02</td>
<td>[47]</td>
</tr>
<tr>
<td>Fe-5Pd</td>
<td>HS</td>
<td>IM</td>
<td>0.074 mg/(cm²d)</td>
<td>0.03</td>
<td>(Huang et al. 2014)</td>
</tr>
<tr>
<td>Fe-5Pt</td>
<td>HS</td>
<td>IM</td>
<td>0.120 mg/(cm²d)</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

*HS... Hank’s solution; SBF... Simulated body fluid; PBS... Phosphate-buffered saline; PD... Potentiodynamic polarization method; IM... Immersion test;*

According to Hermawan et al. [49] the following mechanisms are involved during degradation of Fe–Mn alloys in physiological media (Fig. 1.3A). The initial reaction after immersion of the alloy in the fluid involves the dissolution of the metal (oxidation) given by the two anodic partial reactions (Fig. 1.3A-a):

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1.1)
\]

\[
\text{Mn} \rightarrow \text{Mn}^{2+} + 2e^- \quad (1.2)
\]

In aerated (i.e. oxygen-containing) aqueous solutions in the pH-range between 4 and 10, the reduction of dissolved oxygen is the partial cathodic reaction [20]:

\[
\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2e^- \rightarrow 2\text{HO}^- \quad (1.3)
\]

The partial anodic or cathodic reactions, however, can only proceed as fast as one of the two reactions gets limiting. The dissolved metal ions may further react with hydroxyl ions (HO\(^-\))
forming hydroxide layers (hydrous metal oxides, Fig. 1.3A-b). In the following the reactions are given for the main constituent Fe:

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 \text{ or } \text{FeO.H}_2\text{O} \tag{1.4}
\]

\[
\text{Fe(OH)}_2 + \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \text{ or } \frac{1}{2}\text{Fe}_2\text{O}_3 \cdot \frac{3}{2}\text{H}_2\text{O} \tag{1.5}
\]

From literature is known that the corrosion products of iron in aqueous solutions typically comprise a layered structure: an outermost Fe$_2$O$_3$.nH$_2$O surface layer, an Fe$_3$O$_4$.nH$_2$O layer in the middle, and an FeO.nH$_2$O layer at the bottom [49]. A similar structure has been revealed in many in-vitro studies, where a layer of brownish-red degradation products, indicating the formation of hematite (Fe$_2$O$_3$), has been observed over a black layer reflecting the formation of magnetite (Fe$_3$O$_4$) or wustite (FeO). During the course of degradation, pits on the metal surface emerge (Fig. 1.3B), along with an increased concentration of Cl$^-$ at the degradation surface. Hermawan et al. proposed that Cl$^-$ ions from the immersion media diffuse through the porous oxide layers to the metal surface to compensate for the increased Fe$^{2+}$ or Mn$^{2+}$ concentration (Fig. 1.3A-c). The Cl$^-$ ions may subsequently react with metal ions, according to the following equation:
The metal chloride may also react with water to hydroxide and free hydrochloric acid:

\[
\text{Fe}^{2+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2
\]

As a result the pH decreases locally, leading to the formation of pits. Finally, at a later stage of the degradation process the precipitation of Ca and P-rich layers onto the hydroxide layers occurs (Fig. 1.3A-d). Hermawan et al [49] also remarked in their work that the degradation products were not completely soluble in the test media and that the formation of the oxide layers generated a decrease in the degradation rate.

1.2.4 Biocompatibility considerations regarding Fe and Fe–Mn–Pd alloys

The first step in assessing biocompatibility includes cytological investigations via cell tests. Cytocompatibility studies of Fe [41, 50-53], Fe–Mn [42, 49], Fe–Pd [47], and Fe–Mn–C–(Pd) [54] are reported in literature. In these investigations an acceptable biocompatibility for Fe and Fe-based alloys was confirmed, and it was suggested that these materials be regarded as potential biodegradable implant materials. The next phase in assessing biocompatibility includes animal studies. Table 1.3 gives an overview of various in-vivo studies of Fe reported in literature, the animal model used, the study period, and the main findings.

In the early study by Peuster et al. [3] pure Fe stents were implanted in the descending aorta of New Zealand white rabbits. No early restenosis due to thrombotic processes, no pronounced inflammation reactions, and no local or systemic toxicity were observed. The neointimal\(^1\) proliferation\(^2\) was seen to be comparable with that of standard materials. Similar results were reported in later work by Peuster et al. [4] and Waksman et al. [35] where Fe stents were implanted in the descending aortas of minipigs and juvenile crossbred swine. Promising results were obtained demonstrating the potential applicability of Fe as biodegradable implant material. However, in these investigations [3-5] the stents remained more or less intact up to one year after their placement, implying that the in-vivo degradation rate of Fe is too slow and hence that a higher degradation rate is warranted.

In a more recent study by Pierson et al. [55], Fe wires were implanted in the artery lumen (simulating bioabsorbable stent blood contact) or artery walls (simulating bioabsorbable

\(^1\)Neointima = scar tissue of blood vessels, which forms as a result of stent placement and intima refers to the innermost lining of the blood vessels;

\(^2\)Cell proliferation = cell growth;
Table 1.3. *In-vivo* studies of Fe and an Fe–N alloy in various animal models.

<table>
<thead>
<tr>
<th>System</th>
<th>Animal model/Implantation site</th>
<th>Study period</th>
<th>Findings</th>
<th>Ref. (year)</th>
</tr>
</thead>
</table>
| Fe     | Rabbit; Descending aorta        | 18 months    | • Low thrombogenicity and mild inflammatory response  
|        |                                 |              | • No local or systemic toxicity  
|        |                                 |              | • Increased degradation rate is warranted | [3] (Peuster et al. 2001) |
| Fe     | Minipigs; Descending aorta      | 12 months    | • Fe recommended as suitable biodegradable stent material  
|        |                                 |              | • No local toxicity due to corrosion products  
|        |                                 |              | • No systemic or organ toxicity  
|        |                                 |              | • Faster degradation rate desired | [4] (Peuster et al. 2006) |
| Fe     | Swine; Coronary artery          | 28 days      | • Signs of degradation after 28 days  
|        |                                 |              | • No evidence of thrombosis or enhanced inflammation observed | [35] (Waksman et al. 2009) |
| Fe     | Rat; Abdominal aorta wall and lumen | 9 months  | • Higher degradation at artery wall compared to lumina (matrix contact vs. blood)  
|        |                                 |              | • Degradation products retained in expanded form in the artery wall, which may challenge long-term integrity of the artery | [55] (Pierson et al. 2012) |
| Fe     | Mouse; Tail                     | 9 months     | • Local accumulation of degradation products with no indications of toxic effects  
|        |                                 |              | • Iron accumulation in organs (especially in the spleen) without noticeable indications of inflammation | [56] (Mueller et al. 2012) |
| Fe–N   | Minipigs; Iliac artery          | 12 months    | • Slight luminal loss resulting from intimal hyperplasia and relative stenosis of the stented vessel segment with piglets’ growth were observed by 12 months  
|        |                                 |              | • No thrombosis or local tissue necrosis was found  
|        |                                 |              | • Significantly degraded struts and accumulation of corrosion products were seen by 12 months | [45] (Feng et al. 2013) |

Stent matrix contact) of Sprague Dawley rats. Interestingly it was noticed that the bloodcontacting (lumen) wires experienced a much lower degradation rate compared to the wires pressed against the artery wall, indicating that the implant environment itself has a significant influence. Furthermore, voluminous degradation products, in the form of hematite (Fe$_2$O$_3$), accumulated and were retained in the arterial wall during the study period of 9 months. Critically, it was stated that these expanded degradation products may challenge the long-term integrity of the artery. In the *in-vivo* study by Mueller et al. [56] thin foils of Fe were implanted in the tails of mice, and clear implant fragmentation and gradual degradation during the study period of 9 months were observed. In this work local accumulation of Fe degradation products in the vicinity of the implants was also detected, together with a minor inflammatory response, but with no indication of toxic effects. Feng et al. [45] implanted nitride Fe-stents in the iliac arteries of minipigs for a study period of 12
months. No thrombosis or local tissue necrosis\(^1\) were observed. After 12 months of implantation markedly degraded struts and local accumulation of degradation products were found, accompanied by slight luminal loss of the stented blood vessel due to intimal hyperplasia\(^2\).

In summary, the following may be deduced from the *in-vitro* (degradation and cell tests) and *in-vivo* studies reviewed: Fe–Mn–Pd alloys exhibit an increased *in-vitro* degradation rate compared to Fe; Fe–Mn, Fe–Pd and Fe–Mn–Pd exhibit an acceptable cytocompatibility in cell tests; no toxic reaction in animal studies of Fe (e.g. due to an Fe-ion overdose) occurs; and local accumulation of degradation products (Fe-oxides) takes place. In particular, the latter fact may present a challenge to the use of Fe as biodegradable implant material.

Although much effort has gone into developing Fe-based alloys, in particular steels containing Mn and/or Pd which exhibit an increased *in-vitro* degradation rate compared to Fe, *in-vivo* studies of such materials are lacking. Chapter 6 of this thesis presents *in-vivo* results for Fe and Fe–Mn–Pd alloys in this connection.

### 1.3 Fe–Mn-based-alloys

#### 1.3.1 Phase transformations in the Fe–Mn system

Fig. 1.4a displays the Fe-rich part of the binary Fe–Mn phase diagram. Similar to Ni, Mn is a γ stabilizing element which considerably widens the γ-field. From the binary diagram it is apparent that the γ→α transformation involves significant concentration changes. With increasing Mn-content, the γ→α transformation is constantly shifted towards lower temperatures, and diffusion is increasingly impeded. Thus, under most cooling conditions Fe–Mn alloys containing 4 to 28 wt.% Mn exhibit martensitic transformations. Fig. 1.4b displays the martensite transformation temperatures of Fe–Mn alloys on cooling and the austenite transformation temperatures on heating. In comparison to the Fe–Ni system, where only the γ→α’ transformation upon cooling occurs, in the Fe–Mn system the formation of ε-martenstite is also observed. The transformation temperatures are typically determined by measuring the elongation as a function of temperature in dilatometric experiments. The specific volume of γ is smaller than that of α’-martensite and bigger than that of ε-martensite. Accordingly distinct volume changes can be observed in dilatometric experiments.

---

\(^1\)Necrosis = cell injury resulting in the death of cell through apoptosis;  
\(^2\)Intimal hyperplasia = thickening of the innermost layer of a blood vessel;
14

Fig. 1.4. (a) Fe-rich section of the Fe–Mn phase diagram [6]. (b) Martensitic transformation temperatures for the metastable $\alpha'$- and $\varepsilon$-phases: starting ($M_s$) and finishing ($M_f$) temperatures on cooling, and starting ($A_s$) and finishing ($A_f$) temperatures on heating [6]. (c,d) Elongation as a function of temperature for: (c) Fe-5Mn, and (d) Fe-20Mn. (e)-(h) Light optical micrograph of (d) Fe-9Mn: only $\alpha'$ visible; (e) Fe-13.8Mn: $\gamma$-grey, $\varepsilon$-white laths, $\alpha'$-black needles; (f) Fe-14.5: $\gamma$-bright, $\varepsilon$-dark; (g) Fe-31Mn: only $\gamma$ visible [57].

experiments revealing the occurring phase transformations. Fig. 1.4c,d displays complete heating and cooling cycles of Fe-5Mn and Fe-20Mn alloys. For Fe-5Mn the $\alpha'\rightarrow\gamma$ transformation upon heating is characterized by a pronounced contraction, and vice versa, on cooling the $\gamma\rightarrow\alpha'$ is apparent through a pronounced expansion. It can be seen that the austenite reversion occurs at considerably higher temperatures compared to the martensite reaction. This broad hysteresis allows tempering of the martensitic matrix of Fe–Mn alloys containing 5-10wt.% Mn at quite high temperatures before it transforms back to $\gamma$. For the Fe-20Mn alloy the $\varepsilon\rightarrow\gamma$ transformation is revealed by a volume expansion and, upon cooling, a contraction, indicating the $\gamma\rightarrow\varepsilon$ transformation, as is visible in Fig. 1.4d.

Due to the variety of martensitic transformations, in binary Fe–Mn alloys (<28 wt.% Mn) a complex microstructure may evolve upon cooling from the austenite phase field to RT. Under most technical cooling conditions alloys containing ~4-10 wt.% Mn consist completely of $\alpha'$-martensite, which exhibits a characteristic lath martensitic microstructure (Fig. 1.4e). According to Schumann [10], in alloys containing 10-14.5 wt.% Mn austenite transforms
upon cooling to $\varepsilon$-martensite ($\gamma \rightarrow \varepsilon$), which may further transform to $\alpha'$-martensite ($\varepsilon \rightarrow \alpha'$; Fig. 1.4f). In alloys with an Mn content between 14.5-27 wt.% Mn $\gamma$ partially transforms to $\varepsilon$-martensite (Fig. 1.4g) and steels with more than 28 wt.% Mn remain austenitic upon cooling to room temperature (Fig. 1.4h).

### 1.3.2 Microstructure and mechanical behavior of Fe–Mn alloys with lath martensite

This thesis primarily investigated alloys which contain 5-10 wt.% Mn. These alloys consist completely of $\alpha'$-martensite after quenching from the austenite phase field to RT (Fig. 1.4b). In comparison to carbon steels the unit cell of $\alpha'$-martensite is not tetragonally distorted, and it has a cubic structure [57]. The composition of the quenched-in $\alpha'$-martensite is the same as that of the initial $\gamma$ and hence $\alpha'$-martensite can be regarded as a metastable, supersaturated solid solution. Fig. 1.5 gives an overview of the as-quenched lath martensitic microstructure revealed by means of various microscopy techniques. The typical lath martensitic microstructure is characterized by prior austenite grain boundaries (PAGBs) as

![Fig. 1.5. (a) Light optical micrograph (LOM) of Fe-10Mn. (b) Electron backscatter diffraction (EBSD) orientation map of Fe-10Mn. Prior austenite grain boundaries (PAGBs) and packet boundaries are indicated by dashed and dotted lines, respectively. (c) Transmission electron microscopy (TEM) image of Fe-9Mn [58]. The dashed lines indicate the characteristic lath-shape of the martensite grains. (d) Schematic illustration of the microstructural features [59].](image-url)
the biggest structural units, which are further sub-divided into packets of parallel blocks which also contain a large number of laths (Fig. 1.5d) [9, 59]. A similar characteristic lath martensitic microstructure can be found in various Fe-based alloys, e.g. Fe–Sn, Fe–V, Fe–W, and (importantly here) in Fe–Ni and maraging steels [58-60]. It is commonly considered that the boundaries of blocks and packets are of high-angle type, whereas the boundaries of laths within a block are of low-angle type [9].

![Graphs showing the relation between yield strength and grain size, austenite grain size and martensite packet size, and variation of packet size and block width of lath martensite with prior γ grain size.](image)

Fig. 1.6. (a) The relation between yield strength and grain size for Fe–Mn alloys [58]. (b) Relation between austenite grain size and martensite packet size for Fe–Mn alloys [58]. (c) Variation of packet size and block width of lath martensite with prior γ grain size [61].

For Fe–Mn alloys containing 5 and 9 wt.% Mn Roberts [58] demonstrated that the structural feature equal to the grain size in ferrite is the packet size of the lath-martensite structure. He observed a Hall-Petch relationship for Fe-5Mn and Fe-9Mn alloys in which the grain size is given by the packet size (Fig. 1.6a). He showed further that the packet size decreases as the PAGB size is decreased (Fig. 1.6b). Similar behavior is also revealed for various low-carbon steels exhibiting a lath martensitic microstructure (Fig. 1.6c) [61]. Roberts also observed that the width of the martensite lath is independent of the packet size and Ms-temperature of the alloys. The yield strength for Fe–Mn alloys containing 5 to 10 wt.% Mn varies only a little, and hence the variation in strength due to solid-solution strengthening in this concentration
range is considered relatively small [58, 62, 63]. Holden et al. [62] proposed that solid-solution strengthening for such lath martensitic alloys contributes about 30% of overall strength. The strength of these alloys is given mainly by the high dislocation density [58, 62, 63], which is formed during the martensitic transformation. In lath martensitic steels the dislocation density was reported to be on the order of $10^{14}$ to $10^{15}$ m$^{-2}$ [64]. Binary Fe–Mn alloys containing 5 to 10 wt.% Mn are prone to a kind of temper embrittlement which occurs if the steels are aged in a temperature range between 300 to 500 °C [65-68]. In tensile tests at cryogenic temperatures (Fig. 1.7a) this embrittlement manifests itself in a loss of ductility, or in an increase in the ductile-to-brittle transition temperature (DBTT) and brittle intergranular fracture occurring along the PAGBs (Fig. 1.7b). In low-alloyed steels temper embrittlement is commonly associated with the segregation of impurities such as Sb, Sn and P, weakening the grain boundaries [71, 72]. In contrast, for Fe–Mn alloys the segregation of the main alloying element Mn to PAGBs is given as the reason [67-69]. In this respect Nasim et al. [69] showed by means of Auger electron spectroscopy measurements on an Fe-8Mn alloy that during aging at 450 °C Mn rapidly segregates to the PAGBS (Fig. 1.7c). Similarly, Heo et al. [68] revealed for an Fe-12Mn alloy that the observed grain-boundary embrittlement during aging at 400 °C is a result of Mn segregation to the PAGBs. From a theoretical point of view, Mn on its own was also shown to be an embrittling element in Fe. Using a pair bonding approach (taking the molar sublimation enthalpies and

![Image](image-url)
atomic sizes into account), Seah [70] presented a theory to qualitatively describe the segregation-induced changes in grain-boundary cohesion. He showed that Mn can be regarded as an embrittler in an iron matrix (Fig. 1.7d).

### 1.3.3 Fe–Mn-based maraging steels

Maraging steels are a special class of low-carbon ultra-high-strength steels. They exhibit a characteristic lath martensitic structure in their initial as-quenched state. Their high strength is caused by their high dislocation density and by the formation of nm-sized intermetallic precipitates evolving within the martensitic matrix during aging (Fig. 1.8a,b). The aging treatment is typically performed at around 500 °C. Maraging steels exhibit several desirable properties such as ultra-high strength in combination with good fracture toughness, simple heat treatment with only minimal distortions, good weldability, easy machining behavior, and good corrosion resistance (in stainless grades) [16, 73]. Figure 1.8c presents an overview of the strength-ductility profile of various maraging steels in comparison with other steel families.

![Figure 1.8](image)

**Fig. 1.8.** (a) APT results for a PH 13-8 maraging steel. The red dots illustrate Fe-atoms. The blue spherical regions represent NiAl precipitates which have formed in the Fe-matrix during aging for 12 h at 500 °C [74]. (b) Dark-field micrograph taken using a (022) f.c.c. reflection, revealing homogeneous copper precipitation in the martensite matrix of an PH 17-4 maraging steel, aged for 2 h at 510 °C [75]. (c) Strength-ductility profile of various steels; the symbols indicate the properties of existing high-end maraging steel grades [76].

A variety of maraging alloys were developed in the past, and the classical representatives of this steel family are the so-called 18 wt.% Ni maraging steels. However, these steels contain high amounts of expensive alloying elements, cobalt in particular but also nickel, and much effort has been made to develop cheaper variations such as cobalt-free grades [16, 73]. Mn
is cheaper than Ni, and Fe–Mn alloys feature transformation characteristics which are similar to Fe–Ni alloys and result in the formation of lath martensite under most cooling conditions [10, 77]. Ternary Fe–Mn–Ni alloys also exhibit considerable age-hardening, similar to that of 18 wt.% Ni maraging steels [78]. Hence, to further reduce material costs it was attempted to replace Ni partially or fully with Mn.

Figure 1.9a displays the age-hardening curves for an Fe-6Mn-12Ni alloy [79]. A characteristic single peak-hardening curve typical of maraging steels is visible, and can be basically divided into two regions (Fig. 1.9b): (i) an under-aged region, where the hardness rapidly increases, and (ii) an over-aged region, where the hardness decreases upon aging. The occurrence of a single-peak in the age-hardening curves is a result of the interaction between dislocations and the evolving precipitates. In region I dislocations cut the precipitates and with increasing particle size during aging the resistance for dislocation motions is raised, leading to an increase in strength. Precipitates can impede dislocation motion via different mechanisms. Table 1.4 gives an overview of the various strengthening mechanisms and their underlying equations. In maraging steels coherency (e.g. Fe–Mn–Ni [81]), order-strengthening (e.g. PH 13–8 Mo [82]) or a combination of both (e.g. 18 wt.%Ni maraging steel T-250 grade [83]) are commonly considered to be the governing mechanisms. In region II (over-aged regime) the strength of the material decreases compared to the peak-aged state. This softening is attributed to the Orowan mechanism, where dislocations bypass the precipitates by looping around them, and accordingly an increase in particle size during aging will lead to a decrease
Table 1.4. Different precipitation hardening mechanisms [16]

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Equation for critical resolved shear stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>(2 \cdot G \left( \frac{1}{n} \right)^{1/2} \left( \frac{V_a}{\frac{G}{b}} \right)^{3/2} \left( \frac{f}{T} \right)^{1/2} )</td>
</tr>
<tr>
<td>Stacking-fault</td>
<td>(\alpha (\Delta \gamma)^{3/2} b^{-1/2} (r \cdot f)^{1/2} )</td>
</tr>
<tr>
<td>Modulus</td>
<td>[0.9T_i \left( \frac{\Delta G}{G} \right)^3 \left( \frac{2b \ln \left( \frac{2r}{f} \right)}{f^2 b} \right)^{3/2} (r \cdot f)^{1/2} ]</td>
</tr>
<tr>
<td>Order</td>
<td>[\frac{\gamma_{apb}}{2b^2} \left( \frac{3\pi^2}{32T_i} \frac{f \cdot r}{r^2} \right)^{1/2} \left( 1 - f \right) ]</td>
</tr>
<tr>
<td>Coherency</td>
<td>(4.1 \cdot G f^{3/2} \left( \frac{f \cdot r}{b} \right)^{1/2} )</td>
</tr>
<tr>
<td>Ashby–Orowan</td>
<td>(0.84 \left( \frac{1.2Gb}{2\pi L} \right) \ln \left( \frac{r}{b} \right) )</td>
</tr>
</tbody>
</table>

\(r\)… average particle radius; \(f\)… volume fraction of precipitates; \(G\)… shear modulus (81.6 GPa for Fe); \(\Delta G\)… difference between shear modulus of matrix and precipitates; \(b\)… Burgers vector (0.248 nm for Fe); \(T_i\)… line tension of the dislocation; \(\Delta \gamma\)… difference in stacking fault energy of matrix and precipitates; \(\gamma_{apb}\)… antiphase boundary energy; \(\varepsilon\)… strain energy constant, which can be approximated by \(\varepsilon \approx \frac{2}{3} \left( \frac{a_p - a_m}{a_m} \right)\), with \(a_p\) and \(a_m\) being the lattice constants of the matrix and precipitates, respectively; \(L\)… interparticle spacing, and when assuming spherical precipitates the relation between interparticle spacing, volume fraction of precipitates and average particle radius is given by \(L = \left( \frac{1.23}{\sqrt{3f}} - 2 \right)^{1/3} r \).

in strength. In addition, in maraging steels a reversion of martensite to austenite occurs during over-aging, and is considered to make an important contribution to the loss in strength [73].

In a case similar to Fe–Mn–Ni alloys, Tanaka et al. [80] observed considerable age hardening in the Fe–Mn–Pt system (Fig. 1.9c). This thesis primarily investigated Fe–Mn alloys containing 10 wt.% Mn and 1 wt.% Pd. Ni, Pd and Pt belong to the same group of transition metals in the periodic table. The binary phase diagrams of the Mn–Ni, Mn–Pd, and Mn–Pt systems are also very similar in regard to the occurrence of intermetallic phases. Accordingly Tanaka et al. [80] proposed that in the Fe–Mn–Pd system considerably age hardening may also occur. Chapter 2 below provides deeper insights into the precipitation hardening of Fe-10Mn-1Pd.
Due to the desirable hardening behavior and relatively low costs, Fe–Mn–Ni alloys were intensively investigated in the past. However, it was revealed that they suffer from severe embrittlement when aged in a temperature range between 300 to 500 °C (the same temperature range where precipitation hardening is induced) [79, 84-90] (Fig. 1.10). This embrittlement, similar to that of binary Fe–Mn, is characterized by a loss in tensile ductility (even at RT) and intergranular fracture which occurs along PAGBs (Fig. 1.10a). There is controversy in literature as to the exact source of grain-boundary embrittlement in these hardenable alloys. Besides the segregation of Mn to the PAGBs [79, 84, 86, 87], embrittlement mechanisms related to the evolving particles have been proposed [85, 88-90]. In this context Chapter 5 discusses the mechanical behavior of Fe-10Mn-1Pd upon aging at 500 °C and in particular the local chemistry of the PAGBs.

Overall phase transformations in maraging steels which occur on heating, such as precipitation and reverse martensite to austenite formation ($\alpha' \rightarrow \gamma$), are typically investigated using dilatometry [8]. As an example Fig. 1.11a presents the relative change in length ($\Delta L/L_0$) as a function of temperature for a 350-grade 18 wt.% Ni maraging steel [91]. The first macroscopic contraction corresponds to the formation of precipitates and the subsequent second contraction corresponds to the $\alpha' \rightarrow \gamma$ transformation. For many maraging steels, such as 18 wt.% Ni maraging steel, Fe–Ni–W, and Fe–Mn–Mo (see also Fig. 1.11), it has been observed that the prior precipitation reaction affects the austenite reversion [91-97]. As also visible in Fig. 1.11, upon slow and moderate heating rates the $\alpha' \rightarrow \gamma$ transformation was seen to split into two steps. Kapoor et al. [91] attribute this
Fig. 1.11. (a) 18 wt.% Ni maraging steel (grade 350). Upper graph: Typical plot of relative change in length ($\Delta L/L_0$) vs. temperature indicating the precipitation and martensite to austenite transformations (heating rate = 0.55 °C/s). Lower graph: Corresponding differentiated dilatation curves [91]. (b) The effect of heating rate on dilatometric behavior observed during the heating of a 300-grade 18 wt.% Ni maraging steel [92]. (c) Dilatometric curves recorded at a rate of 0.083 °C/h under a hydrogen atmosphere [95].

splitting behavior to the partitioning of the matrix into solute-rich and solute-depleted regions, enhanced by the prior precipitation reaction. The heating rate within a dilatometric experiment has a considerable effect on the transformation kinetics. In contrast to slow or moderate heating rates, upon fast heating the $\alpha' \rightarrow \gamma$ transformation appears in a single step (Fig. 1.11b). This was ascribed to the absence of precipitation and partitioning of the matrix [91, 92].

Chapter 4 of this thesis discusses in detail the phase transformation which occurs on slow and rapid continuous heating of binary Fe–Mn and ternary Fe–Mn–Pd alloys.

1.4 Atom probe tomography

The basic principle of atom probe tomography is based on the field-emission electron microscope, invented by E. W. Müller in 1935 [98]. Improvements on Müller’s concept
produced field-ion microscopes in 1955 [99] and the first 1-dimensional atom probe in 1967 [100]. However, it was not until 2002 that APT reached the broader materials science community in the form of commercially available instruments (manufactured by the former Imago Scientific Instruments), termed local-electrode atom probe (LEAP) tomographs [101]. The further spread of LEAP instruments was promoted by the implantation of laser pulsing in 2005, which made possible the analysis of non-metallic materials [102]. The scientific contribution of data acquired by atom probe instruments has vastly increased over the last 10 years. This is particularly true in steel research, where the number of published studies employing APT was nearly 20 times higher in 2013 (881) than in 2003 (51), and new insights into nm-scale behavior of steels are expected [103].

Fig. 1.12. (a) Working principle of an atom probe built in the local electrode configuration. (b) Reconstruction process. The point projection provides a relationship between the X,Y coordinates of the detector and the lateral atomic position of the tip surface. The procedure for calculating the z-coordinate includes the following aspects: a) Atoms are field evaporated in a well-defined sequence. b) Assumption that the depth increases incrementally with the number of detected ions. c) To account for the curvature of the tip, corrections are applied. (The figures are adopted from [104])

Fig. 1.12a schematically displays the working principle of a LEAP [104]. Specimens for APT are typically shaped as sharp needles with an apex radius on the order of 20 to 200 nm required for obtaining high electrical fields for field evaporation. For metals, sample preparation can be performed via electropolishing or focused ion beam (FIB) techniques. A high standing voltage is applied to the specimens to induce high electrical fields (~10^{10} V/nm) at the apex. By either applying voltage or laser pulses the surface atoms are

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1 Number of publications in 2003 and 2013 seen on the WEB OF SCIENCE™ (search term “atom probe tomography and steels”).
field evaporated and accelerated towards the position-sensitive detector. The time of ion flight, i.e. the time between a pulse and a hit event on the detector, is measured and used to calculate the mass-to-charge ratio, to identify the chemical nature of the ions. The original positions of the atoms from the specimen are reconstructed based on [105, 106]: (i) the hit position of the ions on the detector \((X,Y)\) is identified by means of a point-projection; and (ii) the evaporation sequence of the ions provides the depth \((Z)\) information (Fig. 1.12b).

**Fig. 1.13.** (a) Trajectory aberration related to the presence of precipitates, resulting in local de-magnification (left) and local magnification (right) [104].

(b) Results from simulation showing the influence on the relative change in apparent precipitate dimension of precipitate size and the difference between the evaporation field of the atoms in the precipitate and matrix [107].

APT has unique capabilities for resolving chemical compositions on an atomic scale. However, it exhibits some artifacts, which arise not only through the imperfect reconstruction procedure but also via experimental effects that lead to deflections in the flight path (trajectories) of the ions. This thesis has analyzed precipitates in particular via APT. In this context, the most well-known artifacts are local magnification or de-magnification effects related to precipitates, which hamper the determination of the exact precipitate sizes (Fig. 1.13a) but in some cases also that of their chemical composition [104]. These trajectory aberrations arise due to differences in the evaporation field of the precipitates and the matrix. In this respect two cases can be distinguished. (i) The atoms of the precipitates exhibit a lower evaporation field; during evaporation the surface of the precipitates will flatten and consequently the ion trajectories will be deflected inwards; this leads to a smaller apparent precipitate size (de-magnification) and a higher apparent density. (ii) The atoms of the precipitates exhibit a higher evaporation field; during evaporation the precipitate will protrude, producing a local increase in curvature, which causes an increase in the apparent precipitate size (magnification) and a decrease in the
apparent density. Based on simulation it was also revealed that these local magnification or de-magnification effects become more pronounced the higher the difference in evaporation fields and the smaller the precipitate dimensions (Fig. 1.13b). However, no general approach exists to correct for these artifacts.

![Fig. 1.14. (A) Atom diagrams illustrating the cluster-finding algorithm: (a) solute atoms (red) in a matrix (white) suggest the presence of a cluster (dashed line); (b) the $D_{\text{max}}$ parameter shown as a green circle positioned above two solute atoms (black) of interest; (c) results of applying the $D_{\text{max}}$ parameter (atoms shown in blue are determined to be part of the cluster) with the size of the envelope parameter ($L$) used to determine potential matrix atoms contained in the cluster, illustrated as the gray circle; (d) shows all matrix atoms (gray) which may be evaluated to determine whether they are contained in the cluster; (e) the erosion distance parameter ($E$) (shown as a purple circle) is applied to all non-cluster atoms to remove atoms around the cluster edges (purple spheres); and (f) the final estimate of the atoms contained in the cluster. (Figure and capitation taken from [108].) (B) Proxigram analysis in an Fe–Ni–Mn–Al alloy. (a) A 25% Ni iso-concentration surface; (b) a specific surface selected for analysis; (c) a 2D illustration of how a proxigram analysis measures the average composition as a function of increasing distances normal to the surface; and (d) the resulting proxigram composition profiles. (Figure and capitation taken from [104].)

There remain a huge variety of methods for analyzing APT data sets, and how the data analysis is performed depends on the region of interest. In this thesis Imago visualization and analysis software (IVAS) from Cameca was used to reconstruct and perform the data analysis, and two main methods were applied: (i) cluster-finding algorithm [108], and (ii) proximity histograms or proxigrams (Fig. 1.14) [109]. Most cluster-finding algorithms use the maximum separation distance and are often applied to identify clusters of only a few atoms or small precipitates. They are based on the fact that the solute atoms in a cluster are closer
together than solute atoms in the matrix. The parameters in the algorithm include $D_{\text{max}}$ (maximum separation distance), $N_{\text{min}}$ (the minimum number of atoms within a cluster) $L$ (envelope parameter); and $E$ (erosion distance). Fig. 1.14A depicts the cluster finding process schematically; [108] recommends guidelines for the choice of appropriate parameters. The proxigram analysis is very powerful because it makes possible the generation of concentration profiles of interfaces with arbitrary geometries such as grain boundaries or precipitates of complex shape, and due to its approach its profiles possess high statistical reliability. Prior to the proxigram analysis, isoconcentration surfaces (surfaces which enclose a region containing a higher concentration of a selected element compared to a chosen threshold value) are created to delineate the region of interest and to serve as reference surfaces for the proxigram calculation. Subsequently discrete shells are generated which follow the shape of the isoconcentration surface with user-defined widths (typically of 0.1 nm) inside and outside the isoconcentration surfaces. Each point in the proxigram then corresponds to the concentration of a shell at a defined distance from the isoconcentration surface (threshold). By convention, the concentrations at negative distances correspond to shells located outside the isoconcentration. Conversely, data points at positive distances are related to concentrations inside the isoconcentration surface. Fig. 1.14B schematically depicts the proxigram analysis method.

More detailed information regarding APT, particularly using LEAP instruments, can be found in recent textbooks [104, 108].

1.5 Aim and outline of the thesis
The aim of this thesis was to investigate the phase transformations and related microstructural and property changes in martensitic Fe–Mn–Pd alloys. Its underlying motivation was the development of a new class of steels intended for application as biodegradable implant material. Accordingly, the thesis also assessed the alloys’ biological performance in animal studies.

The materials investigated were developed according to the design strategy presented in section 1.2. Fe–Mn alloys containing 5 to 10 wt.% Mn with the addition of 1 to 6 wt.% Pd were analyzed, and a main focus was the alloy with 10 wt.% Mn and 1 wt.% Pd (Fe-10Mn-1Pd). All Pd-containing alloys revealed considerable age-hardening, similar to that of maraging steels, which would make it possible to significantly reduce implant dimensions. In
this context phase transformations during isothermal aging at 500 °C and the related microstructural and properties changes were studied in detail. Overall transformation processes upon continuous heating from room temperature up to 1100 °C were also analyzed throughout.

This thesis is a cumulative work, and includes five publications, which are presented in the chapters 2 to 6. Chapter 2 gives a phenomenological description of the precipitation process occurring in Fe-10Mn-1Pd upon tempering between 300 to 500 °C. Microstructural changes were studied in detail via a combination of TEM and APT investigations. Chapter 3 addresses the characterization of the nm-sized hardening phase which evolves during over-aging within the martensitic Fe-10Mn-xPd (x = 1, 3, 6) alloys. Via a combination of dilatometry and thermo-kinetic solid-state simulation, Chapter 4 elaborates a consistent picture of the process involved during the reverse α'→γ transition of binary Fe–Mn and ternary Fe–Mn–Pd alloys. Chapter 5 covers the mechanical performance of Fe-10Mn and Fe-10Mn-1Pd alloys upon isothermal aging. A special focus is the local chemistry of the prior austenite grain boundaries, which were characterized using site-specific atom probe tomography. Chapter 6 describes the outcome of an animal study conducted over 52 weeks, where pins made of Fe and Fe–Mn–Pd alloys were implanted into the femurs of rats. Finally, Chapter 7 summaries the main findings of the thesis and provides a brief outlook.

References


87. N.H. Heo; Ductile brittle ductile transition and grain boundary segregation of Mn and Ni in an Fe-6Mn-12Ni alloy, Scr Mater, 1996, 34, p:1517-1522.


2 Precipitation hardening

A main focus of this thesis was to develop a high-strength material. Precipitation hardening is a common and widespread method to increase the hardness of metals and it plays an import role in modern metallurgy. Chapter 2 phenomenologically describes the pronounced age-hardening behavior of Fe-10Mn-1Pd (in wt.%). It will be shown that this new alloy can be classified as a Ni-free high-strength maraging steel.
Precipitation hardening of biodegradable Fe–Mn–Pd alloys

This work presents a phenomenological description of the precipitation-controlled hardening of a new biodegradable Fe-based alloy developed to fulfill the requirements of temporary implant applications. Pronounced strengthening of the solution-treated martensitic Fe–10Mn–1Pd (in wt.%) alloy upon isothermal aging at temperatures within the ferrite–austenite phase field is observed and attributed to the thermally activated formation of coherent plate-like Pd-rich precipitates on {100} planes of the matrix. The onset and the early stages of alloy decomposition were studied using two complementary techniques: transmission electron microscopy and three-dimensional atom probe analysis. Three distinct regions of the hardening kinetics are recognized and closely correlated to the evolution of the alloy microstructure. Upon aging, clustering of Pd atoms within the Fe–Mn solid solution occurs. The very small clusters grow, coarsen and adopt a plate-like shape, rearranging mutually to reduce the overall elastic strain energy. The elastic interaction of the dislocation substructure with Pd-rich precipitates of evolving morphology affects the dislocation mobility and is responsible for the hardness evolution of the alloy. The study of the hardening kinetics shows that the process exhibits all the features characteristic of maraging steels.

2.1 Introduction

Interest in biodegradable metallic implant materials has been increasing steadily over the past decade. Besides magnesium, which is already well-established as potential material for temporary implant applications [1], iron has become a valid alternative – not least because of its superior mechanical properties. In a recent publication, the potential of currently available Fe-based alloys for temporary implants was summarized [2]. However, because their degradation rate in a physiological environment was found to be too slow, a new biodegradable Fe–Mn–Pd alloy system was developed with a particular focus on adapting the electrochemical performance towards decreased corrosion resistance [3]. Here, the addition of Mn within the solubility limit of iron led to a reduction of the standard electrode potential of the Fe matrix. Minor amounts of Pd were added to generate noble finely dispersed intermetallic phase (IMP) particles, which act as cathodic sites inducing
micrgalvanic corrosion. The combined effect of these two approaches resulted in significantly enhanced corrosion susceptibility making the material attractive for degradable implant solutions [3]. The purpose in selecting Mn and Pd was not only to change the electrochemical properties, but also to improve the mechanical performance. It is well known that binary Fe–Mn alloys (< 28 wt.% Mn) undergo an austenite (γ-phase) → martensite transition upon cooling from the austenite phase field [4], thereby developing a complex microstructure consisting of austenite, α′-martensite and/or ε-martensite domains. By varying the composition and temperature, different deformation modes (slip, twinning, strain-induced phase transitions) can be activated in these alloys [5, 6]. The exceptional variety of mechanical properties can be further adjusted by adding alloying elements to induce either a TRIP (TRansformation Induced Plasticity), or TWIP effect (TWinning Induced Plasticity) [7] or maraging-type behavior. Ternary Fe–Mn–Ni maraging steels where Ni is the main alloying element are well-known to strengthen upon aging at 300–500°C due to the formation of IMP precipitates [8-10]. Raabe et al. recently developed a low-carbon steel containing 9–12 wt.% Mn and minor additions (1–2 wt.% of Ni, Ti and Mo showing the maraging-type behavior and exhibiting strength values of 1500 MPa at good ductility levels [11].

In our previous study [3], pronounced hardening of the biodegradable, low-carbon Fe–10Mn–1Pd steel (in wt.%) was observed upon aging at 500°C. It was suggested that the hardening is due to the formation of fine Pd-rich IMP particles. Detailed microstructural analysis, however, was not an aim of that work and was also largely hampered by the fact that a low-carbon steel was used for alloy production, which prompted the formation of a complex heterogeneous microstructure consisting of α′-martensite, ε-martensite and retained austenite even in the initial solution-heat-treated state. In this work, to study the hardening performance of the Fe–Mn–Pd system, pure iron (Armco) was used for alloy production, because in binary Fe–10Mn (in wt.%) a single-phase microstructure (α′-martensite) forms upon quenching from the austenite phase field [4, 12, 13]. Two complementary techniques, transmission electron microscopy (TEM) and three-dimensional atom probe (3DAP) analysis, were used to study the microstructural evolution of the Fe–10Mn–1Pd alloy upon aging. Various TEM operation techniques were employed to gain microstructural information along the decomposition path on the nanometer scale and to correlate the interaction of the lattice defects with the evolving precipitates to the
hardening behavior of the alloy. Moreover, the 3DAP technique is well-suited for compositional analysis on the nanometer scale, allowing the precipitation process to be followed from the earliest stages of decomposition [14-16].

2.2 Experimental section

Two alloys of nominal compositions Fe–10Mn and Fe–10Mn–1Pd (in wt.%; for the alloy composition in at.% see Table 2.1) were produced from the following raw elements: Fe (Armco), Mn (99.9 %, Alfa Aesar, Germany) and Pd (99.95 %, UBS, Switzerland). The elements were melted in a vacuum-induction furnace under 300 mbar argon atmosphere of purity 99.998 % and cast into a copper mould. To ensure phase homogeneity, the ingots were encapsulated in quartz tubes under 215 mbar argon atmosphere and solution-heat-treated (SHT) for 12 h at 1250°C, followed by water quenching. Isothermal aging of the SHT specimens was performed at 375, 400, 425, 450 and 500°C in air for various durations (up to 11 days), followed by quenching in water.

Table 2.1. Nominal compositions in weight (wt.) and atomic percent (at.) of Pd-free and Pd-doped alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe wt.%</th>
<th>Mn wt.%</th>
<th>Pd wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10Mn</td>
<td>90</td>
<td>10</td>
<td>---</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>89</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

To follow the aging process of the heat-treated materials, Vickers hardness (HV10) was measured using a Brickers 220 hardness tester (Gnehm, Switzerland). Five measurements per specimen state were carried out using an indentation time of 6 s.

Characterization of the fine-scale microstructure of the Fe–10Mn–1Pd alloy was performed by TEM and 3DAP analysis of specimens in four different heat-treated states: solution-heat-treated (SHT); SHT followed by aging at 500°C for 10 min (SHT+500°C/10min); SHT followed by aging at 500°C for 30 min (SHT+500°C/30min), and SHT followed by aging at 500°C for 1800 min (SHT+500°C/1800min). Conventional TEM (CTEM) and high-resolution TEM (HRTEM) were used for morphology and defect structure analysis. The compositional contrast of the evolving heterogeneous material was followed using the atomic-number-sensitive high-angle annular dark-field (HAADF) imaging mode of the scanning TEM (STEM). The TEM specimens were prepared by mechanical grinding of 200 μm-thick disks down to about 100 μm. Out of these, disks with a diameter of 3 mm were punched. These disks were then dimpled on one or both sides with a Gatan dimple grinder with 1 μm diamond suspension (Metadi oil-based). Electron transparency was obtained by further thinning of the foils with a twin-jet electropolisher (TenuPol-5, Struers) operated at 10–12 V dc at -40°C. A solution of 90 vol.% of
methanol and 10 vol.% of perchloric acid served as electrolyte. The TEM studies were performed using a FEI Tecnai F30 machine operating at 300 kV.

For 3DAP analysis, square bars of $0.3 \times 0.3 \times 15$ mm$^3$ were cut from the ingots by spark erosion. To obtain a needle-like specimen shape, the bars were electrochemically polished in a standard two-step procedure [14], using a solution of 25 vol.% of perchloric acid and 75 vol.% of ethanol, followed by polishing in a solution of 2 vol.% perchloric acid and 98 vol.% butoxyethanol. The experiments were performed using a LEAP 3000X HR (Imago Scientific Instruments) under ultra-high vacuum ($<10^{-10}$ mbar) with a pulse fraction of 15% and a sample temperature of 60 K. The SHT+500°C/1800min specimens were measured at 80 K because of their brittleness. Data processing was conducted using the IVAS 3.4.1$^{TM}$ software package (Imago Scientific Instruments).

For phase identification, X-ray diffraction (XRD) measurements (PW 1800, Philips) were conducted using Cu $K_\alpha$ ($\lambda=0.15406$ nm) radiation operating at 45 kV and 40 mA. The quantification of the austenite volume fraction ($V_\gamma$) was carried out as proposed in [17] using the integrated intensity of the 200 and 220 $\gamma$-phase peaks and the 200 martensite diffraction line.

2.3 Results

2.3.1 Hardness measurements

Fig. 2.1. Hardness evolution over time of (a) Fe–10Mn–1Pd and Fe–10Mn aged at 500°C, and (b) Fe–10Mn–1Pd aged at 300–500°C.

Fig. 2.1a presents the variation in hardness as a function of aging time for the Pd-free and Pd-containing alloys aged at 500°C. The alloys show markedly different behavior. For Fe–10Mn, a small increase in hardness after 5 min is followed by a gradual decrease down to a value even lower than that of the SHT state. In contrast, the hardness of Fe–10Mn–1Pd increases drastically from the beginning and reaches a peak value of 462±5 HV10 after only 30 min of aging, yielding a ca. 70% rise as compared to the initial SHT state.
The temperature dependence of the hardening kinetics of Fe–10Mn–1Pd is presented in Fig. 2.1b. Pronounced hardening is observed over a wide temperature range of 300–500°C. With the exception of 300°C, the hardening behavior follows the same pattern at all temperatures and features approximately the same peak hardness value, though for different aging durations. We distinguish three stages in the aging sequence: (i) an underaged region, where hardness increases rapidly; (ii) the peak-hardness range; and (iii) the overaged region, where hardness slowly decreases. For microstructural studies, a temperature of 500°C was chosen as the most convenient from a practical point of view (fast but still easily-measurable kinetics).

2.3.2 Microstructural analysis

Microstructure analysis of the Fe–10Mn–1Pd alloy was performed on specimens in four different heat-treatment states: SHT, underaged (SHT+500°C/10min), peak-aged (SHT+500°C/30min), and overaged (SHT+500°C/1800min).

2.3.2.1 Transmission electron microscopy observations

![TEM micrographs of Fe–10Mn–1Pd in the SHT state. (a) Micrograph showing characteristic martensitic laths of the ferrite matrix. (b) Microstructure of a grain seen in the [001] zone-axis orientation. The grain is strained and a high dislocation density is apparent, with the dislocations arranged in bundles.](image)

The microstructural analysis of the SHT material revealed the characteristic martensitic morphology of the ferrite matrix (Fig. 2.2) with lath-shaped grains of a few micrometers in size (Fig. 2.2a) containing a high dislocation density and small-angle grain boundaries (Fig.
The dislocations are entangled in bundles consisting of long straight dislocation segments. Neither TEM/STEM, nor electron diffraction analysis revealed the occurrence of clustering in the SHT specimens.

The microstructure was found to differ for the alloys in the other three heat-treated states (Fig. 2.3) compared to the SHT state. In the SHT+500°C/10min specimens, the morphology and density of lattice defects were similar to those of the SHT material, but in all SHT+500°C/10min specimens a very high density of specks (see white arrows in Fig. 2.3a) or, at higher magnifications, speck-like contrast modulations (white arrows in Fig. 2.3b), were observed by CTEM in nearly the defect-free areas. The specks are about 2-4 nm in size, are homogeneously distributed within the grains and at higher magnifications reveal a lip-like strain contrast (arrows in Fig. 2.3b). This contrast feature is also known as “Ashby-Brown contrast” [18] and is characteristic of very small coherent precipitates [19, 20]. The actual size of the clusters responsible for this strain contrast could not be determined (also not via HRTEM imaging) but is smaller than the visual size of the specks. It is worth noting that the “lines of no contrast” of all lip-like features in Fig. 2.3b are parallel to each other. In grains of SHT+500°C/10min specimens imaged in higher zone-axes symmetry (for example <100>, <110>), however, the lip-like features were found to be aligned in two perpendicular directions within the same grain, namely the [100] and [010] directions (images not shown).

At the SHT+500°C/10min state, the clusters responsible for the Ashby-Brown contrast did not cause any additional diffracted intensity modulations in the corresponding electron diffraction patterns (see inset). Small islands of Moiré contrast were also found in the TEM images (squares in Fig. 2.3b). These islands have nearly the same size and the fringes within them are aligned along a small number of directions within the same grain. This indicates a definite crystallographic correspondence between two lattices responsible for the islands of Moiré-contrast.

The peak-aged material (SHT+500°C/30min) showed microstructural peculiarities similar to SHT+500°C/10min. No noticeable difference in the number density of the dislocations and lip-like features was found, but the morphology of the dislocations changed considerably. The dislocation lines are shorter than in the SHT+500°C/10min specimens, and jagged (Fig. 2.3c). The most prominent difference is, however, that the lip-like features of the
Fig. 2.3. Bright-field TEM micrographs of Fe–10Mn–1Pd in the (a, b) SHT+500°C/10min, (c, d) SHT+500°C/30min, and (e, f) SHT+500°C/1800min states. (a) Traces of dislocations are seen as black curved lines in the image, acquired in the [113] zone-axis orientation. The short white arrows point to dark specks that
were found everywhere in the specimen. These nm-sized specks are evenly distributed and do not cause additional intensity modulations in the corresponding diffraction pattern (inset). (b) A higher magnification image of another grain in the same orientation shows the morphology of the specks. The lip-like features (indicated by white arrows) are smaller than 4 nm and aligned parallel to each other. The fringes of Moiré contrast in small areas (see white squares) are aligned in a small number of directions within the grain. (c) Numerous lip-like features (see white arrows) are seen in the micrograph acquired in the [102] zone-axis orientation. The diffraction pattern in the inset confirms that the “lips” lie on the (010) plane. Dislocations (curvy black lines) are densely decorated with lip-like features. (d) A higher magnification micrograph from the same grain as in (c). The black arrows point to nearly vertical rows of lip-like features aligned along dislocation lines that are not necessarily visible under these imaging conditions. (e) In the micrograph acquired from a grain in the [001] zone-axis orientation, the Ashby-Brown contrasts (see white arrows) lie along two mutually perpendicular directions, i.e. [010] and [100] (see diffraction pattern of the inset). The higher magnification image in (f) is taken from a thinner area of the same grain and reveals the plate-like shape of the particles. The plates are about 10 nm in size and located mainly at dislocations (black jagged lines in the image). The weak diffuse streaks in the inset (white arrows) confirm the presence of the platelets on (100) and (010) planes of the matrix.

SHT+500°C/30min specimens (white arrows in Fig. 2.3c) are arranged along dislocation lines (black arrows in Fig. 2.3d) and have grown in size (Fig. 2.3c and HRTEM image in Fig. 2.4). The “lines of no contrast” that run between the “lips” (note Fig. 2.3c, d and Fig. 2.4 are acquired in a [102] zone-axis orientation) are parallel to the same direction in the whole grain and according to the corresponding diffraction pattern lie parallel to the (010) planes of the matrix. The diffraction pattern in Fig. 2.3c also corresponds to that of Fig. 2.3d. This indicates a definite crystallographic correspondence between the clusters and the matrix.

The HRTEM image in Fig. 2.4 is acquired from another grain in the [102] zone-axis orientation. It confirms the specific crystallographic relationship between the matrix and the clusters and reveals their actual size and morphology. It is clearly seen from the HRTEM image in Fig. 2.4 that the clusters are sandwich-like plates that lie on (010) planes of the ferrite matrix and are about 5–6 nm long and 1–1.2 nm thick. From the cluster morphology (shape and arrangement) and the strict crystallographic correspondence to the matrix lattice (Fig. 2.3d, Fig. 2.4), it can be concluded that the clusters have developed distinct interfaces which appear to be coherent (and are thus in the following also termed “particles”). However, since misfit dislocations at the interfaces cannot be excluded, the relaxation to semicoherency upon growth of the particles may also have occurred.
Fig. 2.4. HRTEM image of Fe–10Mn–1Pd in the SHT+500°C/30min state. The image is taken in the [102] zone-axis orientation. The lip-like plates are aligned parallel to each other and lie on (010) planes (the white arrow indicates the normal to the (010) plane).

In the specimens annealed at 500°C for 1800 min (Fig. 2.3e,f), the number density of plate-shaped particles was found to be reduced compared to that of the peak-aged alloy state, and their diameter increased to about 10 nm. Fig. 2.3e and f present two micrographs acquired from different regions of a [001] oriented grain at different magnifications. At these imaging conditions, the “lips” were found to be aligned in two mutually perpendicular directions (white arrows in Fig. 2.3e). Electron diffraction analysis (see inset) confirmed that these directions are the [100] and [010] directions of the martensite matrix. The higher magnification image (Fig. 2.3f) shows that the plate-like particles responsible for the “lips” are located in the defect-free areas of the grains and at jagged short-segmented dislocations.

Fig. 2.5 presents TEM images of the overaged specimen (SHT+500°C/1800min). Fig. 2.5a shows an image acquired in an atomic number sensitive STEM operation mode (HAADF STEM), with thin bright lines (see white arrows) corresponding to Pd-enriched plate-like particles. At this evolution stage, the particles were frequently found to be mutually arranged in stacks and piles (see black arrows in Fig. 2.5b). They still maintain coherency with respect to the matrix, which follows from their morphology and electron diffraction analysis (see inset of Fig. 2.3f). The corresponding diffraction pattern in Fig. 2.3f confirms the occurrence of the particles on {100}-type matrix planes. The weak and diffuse streaks due to
the plate-shaped particles on (010) and (100) planes of the matrix lattice are found along [200] and [020] reciprocal lattice directions (see white arrows in the inset of Fig. 2.3f). The bright fringes running diagonally in the insert of Fig. 2.3f are artifacts resulting from the inertia of the CCD camera shutter; the weak spots seen in Fig. 2.3f are also artifacts of an added intensity of two crossing streaks caused by the particles.

![Image](image_url)

**Fig. 2.5.** HRTEM STEM and HRTEM micrographs of Fe–10Mn–1Pd in the SHT+500°C/1800min state acquired from the same grain in [001] zone-axis orientation. (a) The thin bright lines (see white arrows) show that the plates enriched with Pd (the heaviest constituent of the alloy) lie on the (100) and (010) planes of the ferrite matrix. (b) The various geometrical configurations of the thin plates are indicated by black arrows.

2.3.2.2 Three-dimensional atom probe measurements

Fig. 2.6 presents the 3D reconstruction of the atomic positions of Fe, Mn and Pd for specimens in the four heat-treated states. In the SHT state a homogeneous distribution of all elements is detected (Fig. 2.6a). This was further confirmed by a frequency distribution analysis. Table 2.2 summarizes the chemical composition of the SHT material. The errors were estimated by calculating the standard deviation \( s_n = \sqrt{c(1-c)/n} \) based on the total number of atoms \( n \) measured in the analyzed volume [14], where \( c \) is the measured concentration. The measured elemental content of the alloy is in good agreement with the nominal composition.
Fig. 2.6. 3D reconstruction showing atom-maps of Fe–10Mn–1Pd: (a) SHT-state (box size 39 × 75 × 73 nm³); (b) SHT+500°C/10min (box size 78 × 77 × 79 nm³); (c) SHT+500°C/30min (box size 68 × 64 × 64 nm³); and (d) SHT+500°C/1800min (box size 58 × 54 × 53 nm³). Colors correspond to the following elements: Fe in blue, Mn in red and Pd in black.

Inspection of Fig. 2.6b–d evidences the formation of Pd-rich clusters upon aging at 500°C. After 10 min of aging (Fig. 2.6b), a high density of finely dispersed Pd-enriched regions was found to appear, while 30 min of aging (Fig. 2.6c) resulted in much more pronounced Pd segregation. For the SHT+500°C/1800min samples (Fig. 2.6d) large Pd-enriched agglomerates were found. At this stage of decomposition, an enrichment of Mn within the Pd-rich clusters was observed, but no segregation of Fe was detected.
Table 2.2. Chemical composition (in at.%) of Fe–10Mn–1Pd in the SHT state as obtained by 3DAP analysis.

<table>
<thead>
<tr>
<th>Heat-treatment state</th>
<th>Fe</th>
<th>Mn</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHT (~ 2.85 × 10^6)</td>
<td>88.56 ± 0.02</td>
<td>10.71 ± 0.02</td>
<td>0.73 ± 0.005</td>
</tr>
</tbody>
</table>

*TTotal number of ions n considered for the compositional calculations

To gather more information on the Pd-enriched regions, a cluster search algorithm based on the maximum separation method was applied [21]. The required input parameters separation distance (d_max), surrounding distance (L), erosion distance (d_ero), and the minimum number of ions (N_min) were chosen as suggested in Refs. [22, 23]. For all states aged at 500°C, the same set of parameters was used: d_max, L, and d_ero were all set to 0.6 nm and N_min was set to 11. Table 2.3 summarizes the results generated by the cluster search algorithm for the aged specimens.

Table 2.3. Number of detected clusters (N_c), number density (N_d), effective radius (r_eff), volume fraction (f_V) and increase in volume fraction over time (Δf_V/Δt) of the clusters calculated from the cluster search results of aged Fe–10Mn–1Pd specimens.

<table>
<thead>
<tr>
<th>Heat-treatment state</th>
<th>N_c</th>
<th>N_d (#/m^3)</th>
<th>r_eff (nm)</th>
<th>f_V (vol.%)</th>
<th>Δf_V/Δt (vol.%/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHT+500°C/10min</td>
<td>409</td>
<td>20.8 × 10^23</td>
<td>0.96 ± 0.34</td>
<td>1.1</td>
<td>0.11</td>
</tr>
<tr>
<td>SHT+500°C/30min</td>
<td>282</td>
<td>21.7 × 10^23</td>
<td>1.32 ± 0.64</td>
<td>3.9</td>
<td>0.14</td>
</tr>
<tr>
<td>SHT+500°C/1800min</td>
<td>31</td>
<td>3.7 × 10^23</td>
<td>2.33 ± 1.51</td>
<td>4.7</td>
<td>0.00045</td>
</tr>
</tbody>
</table>

To follow the change in the cluster size with progressing aging, for simplicity a spherical particle shape was assumed in the 3DAP analysis, i.e. an effective particle radius r_eff = 3V_c / 4 was used, where V_c is the cluster volume. It can be seen from Table 2.3 that the average r_eff increases continuously with aging time. The large standard deviation of r_eff reflects the broadening of the cluster size distribution. According to Table 2.3, the number density (N_d) does not change significantly for samples aged for 10 and 30 min. However, for SHT+500°C/1800min, a remarkable decrease by a factor of 6 is seen. In contrast, the volume fraction of the clusters (f_V) increases continuously with aging time. The increase of f_V with time (Δf_V/Δt) in the underaged region (between 0–10 min and 10–30 min) is nearly 3 orders of magnitude higher compared to the overaged state (between 30–1800 min, Table 2.3). The clearly decelerated rise in f_V indicates that the volume fraction of the intermetallic phase approaches an equilibrium value.
Table 2.4. Average cluster compositions (in at.%) of Fe–10Mn–1Pd specimens aged for 10, 30 and 1800 min at 500°C calculated from the cluster search results.

<table>
<thead>
<tr>
<th>Heat-treatment state</th>
<th>Fe</th>
<th>Mn</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHT+500°C/10min (26507)(^a)</td>
<td>44.0 ± 0.3(^b)</td>
<td>14.4 ± 0.2(^b)</td>
<td>41.6 ± 0.3(^b)</td>
</tr>
<tr>
<td>SHT+500°C/30min (48848)(^a)</td>
<td>46.4 ± 0.2(^b)</td>
<td>19.5 ± 0.2(^b)</td>
<td>34.1 ± 0.2(^b)</td>
</tr>
<tr>
<td>SHT+500°C/1800min (45408)(^a)</td>
<td>40.7 ± 0.2(^b)</td>
<td>28.8 ± 0.2(^b)</td>
<td>30.5 ± 0.2(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Total number of ions \(n\) considered for the compositional calculations
\(^b\) Standard deviation \(s_n\) estimated from the number of atoms \(n\) in the analysis

The average compositions of the clusters in the three heat-treatment states calculated by the cluster search algorithm are presented in Table 2.4. The average elemental content \((c_i)\) for \(i = \text{Fe, Mn, Pd}\) of the cluster composition was estimated by summing the number of ions \((n_i)\) for element \(i\) over all detected clusters and dividing this value by the total number of ions \((n_t)\) contained in all the clusters \((c_i = n_i/n_t)\). It can be seen that the Pd concentration of the clusters decreases with aging time, while the Mn concentration increases. No pronounced trend can be deduced regarding the Fe concentration.

2.3.2.3 XRD measurements

![XRD spectra](image)

**Fig. 2.7.** XRD spectra of Fe–10Mn–Pd in the SHT state and aged at 500°C for 1800 min, respectively.

The XRD patterns of the Pd-free and Pd-doped alloys in the SHT state showed the same characteristics, revealing only the presence of the body-centered cubic (bcc) \(\alpha'\)-phase, as was also found for Fe–10Mn–1Pd aged at 500°C for 10 min and 30 min (not shown). Only for SHT+500°C/1800min weak austenite signals were detected, in addition to strong \(\alpha'\)-diffraction lines (Fig. 2.7) indicating the formation of about 4 vol.% reverted austenite.
2.4 Discussion

2.4.1 Strengthening behavior

The results of the hardness tests shown in Fig. 2.1a demonstrate clearly that a minor addition of Pd (1 wt.% = 0.5 at.%) leads to pronounced strengthening of Fe–Mn–Pd as compared to the Fe–Mn alloy upon aging. Tempering of binary Fe–10Mn at 500°C caused an initially small increase in hardness followed by a gradual decrease. Nasim et al. [24] reported similar behavior for an Fe–8Mn alloy tempered at 450°C and suggested that the decrease in hardness occurs due to the thermally induced recovery of lath martensite and the beginning of reverted austenite formation. For the same alloy, annealing at 353°C yielded a two-peak aging curve. There, even though the concentrations of C and N in the alloys investigated were in the ppm range (40 and 30, respectively), it was suggested that the first peak resulted from the formation of iron carbide or nitride and the second peak from the formation of manganese nitride. Analogously, the small hardness peak observed in our binary Fe–10Mn specimen upon aging at 500°C could also be caused by the formation of carbides or nitrides. The minor addition of Pd (1 wt.%) to Fe–10Mn has a significant influence on the aging behavior. The characteristics of the hardness evolution in Fe–10Mn–1Pd are remarkably similar to those of maraging steels [17, 25]: a strong and rapid rise at the beginning, a single maximum, and a slow gradual decrease with progressing aging time – despite the fact that the process happens at moderate temperatures of 300–500°C.

In general, the hardening behavior of maraging steels is qualitatively explained by the interaction of secondary phase particles with dislocations. The prompt hardness increase upon aging is associated with the formation of coherent particles within the martensitic matrix and their impeding effect on dislocation motion [17]. Particle–dislocation interaction mechanisms can include modulus hardening, order hardening and coherency hardening that are effective up to a certain particle size, respectively, before softening initiates [17]. Softening of the material observed at longer aging times is commonly attributed to the Orowan process (i.e. the dislocation motion is accompanied by the formation of dislocation loops around the particles) and to the reverse martensite to austenite transformation. However, taking into account that the Orowan process does not occur before the particles lose coherency with the matrix [17], softening mechanisms for coherent particle systems have also to be considered. The coherent strain hardening model, for example, predicts an increase in strength up to a critical particle size followed by a decrease in strength upon
further growth of the coherent particle [26]. As presented in [17], this critical particle size is smaller than the size when the particle loses coherency. Consequently, coherency strengthening is always followed by coherency softening before Orowan softening takes place. Since the particles in the overaged state (SHT+500°C/1800min) still maintain coherency with the matrix and are quite small, the Orowan process is not considered to be the controlling mechanism in our material.

The decelerated decomposition kinetics at lower aging temperature simply results in a translation of the hardness curve to the right along the logarithmic time scale (Fig. 2.1b). The maximum hardness obtained thereby is independent of the aging temperature. This allows us to conclude that the same hardening mechanism operates at the various aging temperatures. Thus, the different stages of the same process can simply be studied by choosing convenient aging parameters for obtaining distinct microstructures and phase states in the material. At low temperature, the hardening process is slow enough to resolve the effects occurring at the earliest stages of aging. The S-shaped age-hardening curves at 375, 400 and 425°C in Fig. 2.1b indicate three sub-hardening regimes. It is assumed that the initial linear increase in hardness results mainly from the increase in cluster number density ($N_d$) which dominates at this hardness evolution stage. The subsequent strong slope change occurs when saturation of the nucleation sites is reached and particle growth is the main dominating contribution to hardness evolution. Finally, a plateau establishes when particle coarsening dominates.

The activation energy for the early stage of decomposition was obtained from the data in Fig. 2.1b using an Arrhenius plot analysis [27, 28]:

$$\frac{1}{t} = k_0 \exp \left( -\frac{Q}{RT} \right)$$  \hspace{1cm} (2.1)

where $t$ is the time to reach a specific hardness level, $k_0$ is a constant, $Q$ is the activation energy, $T$ is the absolute temperature and $R$ is the ideal gas constant. Fig. 2.8 shows the Arrhenius plot of the inverse time necessary to reach a hardness increase of $\Delta H = 80$ HV10 (compared to the SHT state) versus inverse aging temperature. The obtained activation energy is $159 \pm 8$ kJ mol$^{-1}$. This value is much lower than the one found for the diffusion of Mn in $\alpha$-Fe (251 kJ mol$^{-1}$, [29]) or the self-diffusion of Fe in $\alpha$-Fe (239 kJ mol$^{-1}$, [30]).
Fig. 2.8. Arrhenius plot of the reciprocal time required to reach a hardness increase of $\Delta H = 80$ HV10 ($t_{HV = 80}$) versus inverse temperature for Fe–10Mn–1Pd. The activation energy ($Q$) and the regression coefficient ($r$) of the least square fit (dashed line) of the presented data (black dots) are also displayed.

However, the value is similar to that found for precipitation reactions in Fe–Mn–Ni maraging steels, e.g. Fe–19.5Ni–5Mn (172 kJ mol$^{-1}$, [10]), Fe–12Ni–6Mn (128 kJ mol$^{-1}$, [31]), or for stainless precipitation hardening (PH) steels such as PH 13-8 Mo (139 kJ mol$^{-1}$, [27]). The high reaction rate of the precipitation and the low corresponding activation energies in these systems are normally attributed to nucleation of intermetallic particles at dislocations supported by pipe diffusion [17].

### 2.4.2 Microstructure

In the SHT state, the Fe–10Mn–1Pd alloy consists of a single phase ($\alpha'$-martensite), exhibiting the same typical lath-shape martensite microstructure as reported for binary Fe–10Mn alloys [12, 32, 33]. This confirms that Pd does not affect the SHT microstructure. It is worth noting that the same kind of microstructure is characteristic of industrially important 18 wt.% Ni maraging steels [12, 13, 24].

Upon aging, decomposition initiates. As observed in TEM and 3DAP studies, a large number of small, homogeneously-distributed Pd-rich clusters appear in the SHT+500°C/10min specimens, accompanied by a significant increase in alloy hardness. It is assumed that the strengthening is caused by both an overall increase of elastic strain energy due to the establishment of the coherent cluster-matrix system and the reduction of dislocation mobility due to the interaction of dislocations with the small clusters. An estimated cluster size of 2–4 nm was confirmed by both investigation techniques.
Upon aging for 30 min (SHT+500°C/30min), the clusters grow to about 5–6 nm in diameter and adopt a well-defined plate-like shape. The discrepancy in the estimated cluster diameter between TEM and 3DAP data (Fig. 2.4 and Table 2.3) can be explained by the simplified assumption of a spherical cluster shape in the 3DAP analysis. The particles are enriched in Pd and were found to be arranged along dislocation lines. We assume that this arrangement occurs because of pipe diffusion of Pd atoms along the dislocation cores. Precipitation assisted by pipe diffusion is also a well-known phenomenon in many maraging steels [25, 34]. Moreover, such a particle arrangement is favorable since the coherency stresses at the particle-matrix interfaces become partially relaxed if a particle arrives at a dislocation. As a result, the particle-dislocation system stabilizes and the overall strain energy reduces. The jagged and short-segmented dislocations found in the peak-aged specimens (Figs. 2.3c,d) demonstrate that the particles have a much stronger effect on the dislocation morphology at this evolution stage than in the underaged material. The occurrence of that pronounced dislocation pinning by coherent particles is considered to be very significant and as an effect also valid for the material under stress, despite the fact that TEM analysis was carried out on undeformed material.

In the overaged state (SHT+500°C/1800min) the plate-shaped particles have grown further and are about 10 nm in diameter. This growth is accompanied by an increase of the particle volume fraction (Table 2.3), which illustrate a continuous Pd diffusion from the matrix towards the particles. The TEM and 3DAP observations agree well on the distinct reduction in the particle number density compared to the under- and peak-aged states, reflecting the process of particle growth and coarsening. This evidently contributes to the reduction in the materials strength. Here, dislocation segments between the pinning points become longer (compare Figs. 2.3f and 3d) and can bow out when the specimen is strained. Again, though TEM analysis was performed on the undeformed material, the pronounced change in dislocation morphology upon aging correlates well with the particle evolution and with the changes in the character of the particle-dislocation interaction. As such, the change in dislocation morphology is considered to be the dominating contribution responsible for the strengthening behavior of the alloy.

In addition, the particles rearrange and form stacks and piles (see Figs. 2.3f, 2.5b). This can be attributed to the fact that as the particle size increases the coherency stresses at the particle-matrix interfaces rise. To accommodate the elastic strain the particles re-arrange,
and thus contribute to the softening of the material. In addition, it is also known that the formation of reverted austenite in maraging steels causes softening [25]. The formation of about 4 vol.% reverted austenite was detected by XRD analysis in the overaged alloy (SHT+500°C/1800min) (Fig. 2.7), but no austenite was found in TEM in either of the specimens. This small amount of austenite is not considered to be significant enough to cause the hardness drop in the overaged specimen compared to the peak age state, but may contribute to some extent.

Decomposition behavior similar to that observed in this study has also been reported for a Fe–19.5Ni–5Mn maraging steel [10, 35]. There, aging at 500°C for 10 h generated plate-shaped 0-NiMn precipitates, which also have three sets of {100} habit plane variants. However, compared to our findings, their 0-NiMn plates are much bigger and exhibit a diameter of 35–100 nm and a thickness of 8–15 nm.

Considering Table 2.4, it follows that, upon aging, the average Pd concentration of the clusters decreases, while that of Mn increases. It can thus be assumed that clusters highly enriched in Pd form first within the Fe–Mn solid solution, accompanied by an increase in elastic lattice strain. The accommodation of strain can be facilitated by a Mn-enrichment of the Pd-rich zones. Here, it must be taken into account that for cluster sizes smaller than 1 nm (corresponding to only about 40 atoms) the solute concentration analysis may yield an overestimated value due to the difficulty for the algorithm to ascribe a detected ion either to the matrix or to the cluster [36]. It is not clear whether the reduction in the clusters’ Pd content during aging actually occurs or if it is just a result of uncertainties in the evaluation algorithm. In any case, the participation of Mn in the precipitation sequence is evident (Fig. 2.6d) and its possible stabilizing effect on the formation of the metastable Pd–Mn or Pd–Mn–Fe phase is suggested. This material behavior is very similar to that reported for Fe–20Ni–3.23Mn (wt.%) [35], Fe–12.8Ni–6.68Mn [37] and other Fe–Ni–Mn alloys [8]. There, only in the presence of Mn in the alloy was a hardening effect observed, which was attributed to the formation of NiMn intermetallic phases.

2.5 Summary and conclusion

In this study, we reported on the pronounced hardening of a solution-heat-treated Fe–10Mn–1Pd (in wt.%) alloy upon aging in the ferrite–austenite phase field (300–500°C) exhibiting features characteristic for maraging steels. By complementary TEM and 3DAP
studies, we identified a precipitation sequence upon aging of the material which comprises a high number of nm-sized Pd-rich clusters that evolve into coherent plate-like particles on \{100\} planes of the matrix. The interaction of dislocations with the evolving particles affects and controls the hardening behavior of the material, and thus the precipitation sequence correlates closely with the hardening evolution. The activation energy of the early stages of decomposition (determined to be 159 kJ/mol) coincides well with values of other maraging or PH-steels [10, 27, 31].

Various similarities of our newly developed Fe–10Mn–1Pd alloy with maraging steels were found: (i) the initial (SHT) microstructure of Fe–10Mn–1Pd is markedly similar to that of widely studied 18 wt.% Ni maraging steels [12, 13, 24]; (ii) the aging behavior of Fe–10Mn–1Pd is very close to that seen in maraging steels [17, 25]; and (iii) the precipitation sequence of our material is very close to that known for Fe–Ni–Mn systems [8-10, 31, 35, 37]. Based on this it can be concluded that we have developed a new high-strength Ni-free maraging steel. Moreover, the potentially attractive electrochemical and biological characteristics in combination with its tailorable mechanical performance make the material interesting for a wide range of applications and for biodegradable implants, in particular.

Acknowledgements

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References


3 Precipitation sequence

In Chapter 2 it was shown for Fe-10Mn-1Pd, that during isothermal aging coherent Pd-rich cluster form in the under-aged regime, which upon subsequent aging grow (peak-aged), coarsen (over-aged) and adopt a plate-like shape. In the following Chapter 3 the precipitates appearing in the over-aged material state, of the alloys Fe-10Mn-xPd (x = 1, 2, 6), are characterized regarding their structure and chemical composition.
Structural and chemical characterization of the hardening phase in biodegradable Fe–Mn–Pd maraging steels

Fe–Mn–Pd alloys are promising candidates as biodegradable material for use in temporary implant applications. In this study the hardening phase of Fe-rich martensitic alloys containing 1, 3, and 6 wt.% Pd and a fixed Mn content of 10 wt.% were investigated. All alloys show considerable age-hardening upon isothermal aging at 500 °C exhibiting a behavior characteristic of maraging steels. Atom probe tomography (APT) and X-ray diffraction (XRD) measurements were performed to characterize the composition and crystallography of nm-sized precipitates forming in the over-aged region of the Fe–Mn–Pd alloys. The precipitates consist mainly of Mn and Pd and the peaks of the intermetallic particles observed in the XRD spectra can be ascribed to the face-centered tetragonal $\beta_1$-MnPd phase. The precipitation sequence for Fe–Mn–Pd is revealed to be similar to that reported for Fe–Mn–Ni and Fe–Mn–Pt maraging steels.

3.1 Introduction

Biodegradable metals have received significant scientific interest in recent years and Fe-based alloys are considered promising candidates [1, 2]. In animal studies the potential of pure Fe was evaluated and it was noted that the main drawback of Fe is its slow in-vivo degradation rate [3-5]. According to a design strategy based on metallurgical, electrochemical and toxicological considerations, Schinhammer et al. [2] developed novel biodegradable Fe–Mn–Pd steels. These alloys were found to exhibit increased in-vitro degradation rates compared to pure Fe. Furthermore, an appropriate biocompatibility was evaluated in cytotoxic investigations of Fe–Mn [6], Fe–Pd [7], and Fe–Mn–C–(Pd) [8] alloys. In addition to enhanced degradation rates, high mechanical strength would also be beneficial, so that smaller implant dimensions can be used and thus less material needs to degrade. In the case of Fe-based alloys maraging steels reveal ultra-high strength, which is based on the formation of intermetallic precipitates forming in the martensitic matrix during an aging treatment at temperatures between 300 and 500 °C [9]. Moszner et al. [10] observed that the martensitic alloy Fe-10Mn-1Pd (in wt.%) exhibits all features characteristic of maraging steels and that considerably age-hardening is achieved through the formation of

nm-sized precipitates rich in Mn and Pd. For this alloy an interesting combination of strength and ductility was observed in the over-aged state (see Fig. 3.1). Thus, the potentially attractive electrochemical and biological characteristics, in combination with the suitable mechanical performance, make the material very interesting for biodegradable implant applications. For further alloy optimization the structural and chemical nature of the precipitates, in particular in the over-aged state, is, however, of significant interest.

It is known that the iron-rich martensite alloys of the ternary systems Fe–Mn–Ni and Fe–Mn–Pt also exhibit a maraging behavior [10-12]. Due to its technological relevance the Fe–Mn–Ni system has been extensively studied [11, 13-22], and for this system the precipitation sequence suggested can be summarized as follows: (i) in the initial aging stage the formation of coherent NiMn body-centered-cubic (bcc) zones (A2 or B2) takes place [11, 14, 18]; (ii) at later stages of aging (over-aged region) 0-NiMn intermetallic precipitates with a face-centered tetragonal (fct) structure form [13-15, 17, 18, 20] (however, Kardonskii et al. [11] proposed the formation of Ni$_3$Mn and Singh et al. [22] the formation of bcc NiMn); and (iii) on prolonged aging the precipitates re-dissolve and the final equilibrium microstructure only consists of austenite and ferrite (or martensite) [14]. For the Fe–Mn–Pt system Tanaka et al. [12] proposed a similar precipitation sequence, i.e. the formation of coherent bcc PtMn zones (B2) at the initial stages of aging and ordered fct β$_1$-PtMn intermetallic precipitates in the over-aged regime [12]. In contrast to the Fe–Mn–Ni system the dissolution of the particles on prolonged aging was not observed for the Fe–Mn–Pt alloys, which was ascribed to the higher bonding affinity of Mn with Pt [12, 23]. In the Fe–Mn–Pd system we suggested [10] the formation of coherent zones rich in Mn and Pd in the initial stages of aging. However, the structure of the precipitates in the over-aged state has yet not been clarified, which is our aim in the present work.

For this reason, alloys with a Pd concentration of 1, 3, and 6 wt.% and a fixed Mn content of 10 wt.% were studied. The steels were isothermally aged at 500 °C and the mechanical properties as a function of aging time were investigated. The crystallography of the evolving precipitates was characterized by X-ray diffraction (XRD), and atom probe tomography (APT) was performed to analyze their chemical composition.
3.2 Experimental procedure

Casts of 80 g were prepared from pure elements (Fe: Armco; Mn: 99.9% pure, Alfa Aesar, Germany; Pd: 99.95% pure, UBS, Switzerland) by vacuum induction-melting under argon atmosphere. Prior to the homogenization treatment the ingots were encapsulated in quartz tubes also under argon atmosphere. The solution-heat-treatment (SHT) of Fe-10Mn-1Pd was performed at 1250 °C for 12 h\(^{10}\), and for Fe-10Mn-3Pd and Fe-10Mn-6Pd at 1400 °C for 1 h under argon atmosphere, followed by water quenching. The higher SHT temperature for the steels containing 3 and 6 wt.% was chosen because SEM investigations of Fe-10Mn-3Pd revealed that such a temperature is required to obtain a homogenous microstructure. Isothermal aging of the SHT specimens was conducted at 500 °C in air for various durations (up to 1200 h), followed by quenching in water. Prior to aging of the samples for 1200 h at 500 °C they were sealed in quartz tubes under argon atmosphere to prevent oxidation. To follow the aging process of the heat-treated materials Vickers hardness measurements were performed using a Brickers 220 hardness tester (Gnehm, Switzerland).

For the preparation of tensile test specimens of Fe-10Mn-1Pd an ingot of 1 kg was prepared which was forged and swaged to produce rods having a diameter of 6 mm [24]. The final SHT of this material was conducted at 1150 °C for 12 h under argon atmosphere followed by water-quenching. Stress-strain curves were recorded via standard [25] tensile testing (Schenck-Trebel, Germany), using cylindrical specimens of 2 mm diameter with a gauge length of 12 mm at a strain rate of \(10^{-3} \text{s}^{-1}\).

The microstructure of Fe-10Mn-xPd (x = 1, 3, 6) samples etched with 1 vol.% nitric acid in water was investigated using optical microscopy (OM, Reichert-Jung Polyvar met), and scanning electron microscopy (SEM) was performed with a Hitachi SU-70, equipped with an X-max energy-dispersive X-ray (EDX) detector (Oxford Instruments). For phase identification, XRD measurements (PANalytical, X′Pert Pro) were conducted using Cu K\(_\alpha\) (\(\lambda = 0.15406 \text{ nm}\)) radiation, operating at 45 kV and 40 mA with a step size of 0.03°, a time interval of 12 s, and a diffracted beam monochromator to reduce fluorescence effects. Specimens of all alloys aged for 30 h at 500 °C were analyzed via APT. For this, bars of 0.3 × 0.3 × 15 mm\(^3\) were cut from the aged ingots and needle-shaped specimens were obtained by electrochemical polishing via a standard two-step process [10, 26]. The APT measurements of Fe-10Mn-1Pd were conducted on a LEAP\textsuperscript{TM} 3000X HR ( Cameca) in voltage mode using a specimen temperature of ~80 K, a pulse fraction of 15%, and a constant detection rate of 0.5%. For the alloys Fe-10Mn-3Pd and Fe-10Mn-6Pd the APT experiments were performed on a LEAP\textsuperscript{TM} 4000X HR ( Cameca) in laser mode (355 nm wavelength), because premature failure of the specimen occurred with voltage pulsing. The measurements were conducted using a laser energy of 100 pJ, a specimen temperature of ~24 K, and a constant detection rate of 1%. Data processing was performed using the IVAS 3.6.6 software package ( Cameca) [27].
3.3 Results and discussion

3.3.1 Mechanical properties

Fig. 3.1. Engineering stress-strain curves of Fe-10Mn-1Pd in the initial solution-heat-treated (SHT) state and after isothermal aging at 500 °C for 30 min (peak-aged) and 30 h (over-aged) [24]. A ductile behavior is seen in the SHT condition and in the over-aged case. The yield strength of the alloy in the over-aged state (1076 ± 6 MPa) is much larger than that of the SHT state (662 ± 13 MPa). Brittle failure results for the material in the peak-aged condition. The insert shows SEM pictures of fracture surfaces from the tensile specimens of the alloy in the peak-aged (1) and over-aged (2) conditions. Intergranular fracture, which occurs along prior austenite grain boundaries, is visible in the peak-aged state, and a ductile dimple fracture is apparent in the over-aged case.

Figure 3.1 shows results from tensile tests of Fe-10Mn-1Pd after isothermal aging at 500 °C for different times. In the initial as-quenched condition (solution-heat-treated, SHT) the alloy exhibits a ductile behavior, but brittle failure results in the peak-aged state. However on prolonged aging, i.e. in the over-aged regime, ductility recovers again and the alloy exhibits a similar uniform elongation compared to the SHT condition. The peculiarity of embrittlement and de-embrittlement is discussed in more detail by Moszner et al. [24]. Besides that, the yield strength of the material is considerably increased from 662 ± 13 MPa in the as-quenched condition to 1076 ± 6 MPa in the over-aged state. Thus an interesting combination of strength and ductility results in the over-aged condition and smaller implant dimensions can be achieved in that case.

Figure 3.2 presents age-hardening curves for Fe-10Mn-xPd (x = 1, 2, 6), which were isothermally aged at 500 °C for time periods ranging from 5 min up to 1200 h. All alloys show
significant age-hardening. The higher the Pd content of the alloys, the higher is the resulting peak-hardness, which shows clearly that Pd participates in the strengthening process. The hardness evolution of the alloys, i.e. a fast increase in hardness until the peak hardness is reached followed by a slow decrease on prolonged aging, is typical of maraging steels [9, 10].

Fig. 3.2. Hardness as a function of aging time at 500 °C, revealing age-hardening behavior of the alloys investigated, which is typical of maraging steels. The heat-treatment states used for the XRD and APT measurements are indicated by black arrows and stars, respectively.

3.3.2 Optical microscopy

Figure 3.3 presents optical micrographs of the materials in the SHT condition and after aging for 30 h at 500 °C (over-aged) for comparison. The SHT specimens containing 1 and 3 wt.% Pd (Fig. 3.3a,c) exhibit the typical lath-martensitic microstructure known from binary Fe–Mn alloys containing 4-10 wt.% Mn [28, 29]. SEM investigations of Fe-10Mn-1Pd revealed that the SHT temperature of 1250 °C was sufficient to produce a supersaturated solid solution with a homogenous single phase microstructure [10]. However, for the steel containing 3 wt.% Pd the formation of a single-phase microstructure required a homogenization treatment at 1400 °C (Fig. 3.3c). For Fe-10Mn-6Pd annealed at 1400 °C a coarse two-phase microstructure is revealed in the optical microscopy images (Fig. 3.3e). The dominating phase exhibits the characteristic lath-martensitic structure similar to Fe-10Mn-1Pd or Fe-10Mn-3Pd, while the second phase (dark-contrast in Fig.3.3e) was only found along some prior austenite grain boundaries. The insert to Fig.3.3e shows a backscattered electron image of that phase, also revealing a chemical contrast. A lamellar-like structure is visible, and the bright areas are
Fig. 3.3. Optical micrographs of the alloys in the SHT condition and after aging for 30 h at 500 °C: (a,b) Fe-10Mn-1Pd (SHT at 1250 °C). The inserts show magnified sections, where a finer microstructure inside the prior austenite grains is apparent for the specimen in the over-aged state; (c,d) Fe-10Mn-3Pd (SHT at 1400 °C); (e,f) Fe-10Mn-6Pd (SHT at 1400 °C), etched in 1% HNO₃ in water. The insert in (e) shows a backscattered electron image of the intergranular phase with dark contrast in the optical micrograph. The typical lath-martensitic microstructure is visible for the alloys containing 1 and 3 wt.% Pd. For Fe-10Mn-6Pd, a two-phase microstructure is visible with the lath-martensitic structure dominating.

enriched in Pd and Mn. The image indicates partial remelting of the austenite grains due to overheating slightly above solidus, i.e. quenching from the austenite–liquid two-phase field [30, 31]. Nevertheless, a homogenous distribution of the alloying elements and a high level
of Pd supersaturation can be assumed in the dominating martensitic phase. This results in a higher degree of hardness upon isothermal aging (Fig. 3.2) and hence a higher volume fraction of the evolving precipitates, which also generates stronger signals from the precipitates in XRD measurements facilitating their phase identification. Compared to the specimen in the SHT condition, during over-aging a finer microstructure inside the prior austenite grains was observed for the alloys investigated (Fig. 3.3). This can ascribe to the formation of reverted austenite [15] and was in particular apparent for Fe-10Mn-1Pd (inserts of Fig. 3.3a,b). Table 3.1 summarizes the chemical compositions of the alloys determined via EDX-point measurements.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe wt.%</th>
<th>Fe at.%</th>
<th>Mn wt.%</th>
<th>Mn at.%</th>
<th>Pd wt.%</th>
<th>Pd at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10Mn-1Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nominal</td>
<td>89</td>
<td>89.3</td>
<td>10</td>
<td>10.2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>EDX</td>
<td>88.6</td>
<td>88.8</td>
<td>10.4</td>
<td>10.6</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe-10Mn-3Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nominal</td>
<td>87</td>
<td>88.1</td>
<td>10</td>
<td>10.3</td>
<td>3</td>
<td>1.6</td>
</tr>
<tr>
<td>EDX</td>
<td>86.5</td>
<td>87.7</td>
<td>10.3</td>
<td>10.6</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe-10Mn-6Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nominal</td>
<td>84</td>
<td>86.3</td>
<td>10</td>
<td>10.5</td>
<td>6</td>
<td>3.2</td>
</tr>
<tr>
<td>EDX</td>
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<td>86.0</td>
<td>9.9</td>
<td>10.4</td>
<td>6.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3.3.3 Atom probe tomography

The APT experiments were conducted to analyze the chemical composition of the precipitates and hence to support the results of the XRD measurements (see later). Specimens of the alloys in the over-aged regime (after aging for 30 h at 500 °C) were investigated via APT. This condition was chosen in particular, as Moszner et al. [10] observed for Fe-10Mn-1Pd that in this state the volume fraction of the precipitates did not increase any more with progressive aging-time (∆f_V/∆t), indicating that f_V has approached an equilibrium value. In addition, the size of the particles was still small enough to fully enclose a few of them in the volume detectable by APT. To illustrate the APT results, cylinders of the same dimension (Ø = 38 nm, height = 40 nm) were cut out of the individual reconstructed volumes. Figure 3.4a presents the atomic positions of Fe (green), Mn (red), and Pd (blue). Enrichment of Mn and Pd at the same areas is clearly visible for all specimens investigated. The composition of the precipitates was determined using the proximity histogram (or
Fig. 3.4. (a) 3D reconstruction of Fe-10Mn-xPd alloys (x = 1, 3, 6) after aging for 30 h at 500 °C, showing the atomic positions of Fe (green), Mn (red), Pd (blue), and isoconcentration surfaces for regions containing > 35 at.% Mn+Pd (orange). (b) Proxigrams for Fe, Mn, and Pd corresponding to Mn+Pd isoconcentration of 35 at.%. The dashed black lines indicate the data points used to evaluate the composition of the matrix (C_{Matrix}) and of the precipitates (C_{Prec}). The total number of atoms considered for the concentration measurement of the matrix (N_{Matrix}^t) and the precipitates (N_{Prec}^t) is listed. For all alloys the precipitates are nearly free of Fe and mainly consist of Mn and Pd, indicating that a Mn–Pd intermetallic phase has formed.
proxigram) method [32]. Isoconcentration surfaces [32] (surfaces enclosing a region containing a higher concentration of a selected element compared to a chosen threshold value) were created to delineate the precipitates and to serve as reference surface for the proxigram calculation Fig. 3.4a. In a second step discreet shells with widths of 0.1 nm inside and outside of the isoconcentration surfaces were generated. Each point in the proxigram then corresponds to the concentration of a shell at a defined distance from the isoconcentration surface. By convention, the concentrations at negative distances correspond to shells located outside the isoconcentration surface, which can be employed to evaluate the matrix composition. Vice versa, data points at positive distances are related to concentrations inside the isoconcentration surface and hence can be used to assess the composition of the precipitates. Figure 3.4b presents the results of the proxigrams (only precipitates fully enclosed within the reconstructed volume were considered) for the investigated specimens aged for 30 h at 500 °C. The proxigrams were calculated using an isoconcentration surface of Mn+Pd set to a threshold value of 35 at.% (average inflection point of the Mn+Pd concentration taking into account the three datasets). The black dashed lines in the proxigrams indicate the data points used to calculate the concentration of the elements within the matrix (C\text{Matrix}) and within the precipitates (C\text{Prec}), and the corresponding values are depicted in each graph. According to Miller et al. [26] the concentration in at.% of each element (C_i) was calculated by C_i = N_i / N_t, where N_i is the number of atoms of the corresponding species i and N_t is the total number of atoms considered. The errors were estimated by the standard deviation \sigma_i = \sqrt{C_i(1 - C_i) / N_t}. Similar concentration profiles were obtained for all three alloys. The Pd content of the matrix nearly decreases to zero, reflecting the fact that most of the Pd is confined within the particles. The precipitates are nearly free of Fe and mainly consist of Mn and Pd, thus indicating a Mn–Pd intermetallic character of the hardening phase. According to the binary Mn–Pd phase diagram [33], two intermetallic phases, \beta and \beta_1, can be considered here with respect to the measured composition of the precipitates. Both phases exist over a wide compositional range (\beta = 39 \leq \text{Pd at.\%} \leq 66, \beta_1 = 47 \leq \text{Pd at.\%} \leq 68), at which \beta only occurs above 540 °C while \beta_1 also exists below that temperature. However, Okamoto [33] noted that the true equilibrium phase diagram is still unknown and hence the exact boundaries of the phases need to be considered with care.
3.3.4 X-ray diffraction

Figure 3.5 displays the XRD patterns of the alloys investigated in the SHT state, and subjected to aging at 500 °C for 30 h and 1200 h. In the SHT condition the samples containing 1 and 3 wt.% Pd only reveal the presence of bcc diffraction lines. For Fe-10Mn-6Pd, in addition to strong bcc reflections a weak peak at around 40.2° is visible (insert in Fig. 3.5a), which can be ascribed to the observed intergranular second phase (Fig. 3.3c). Since the specimen was rapidly quenched from 1400 °C the weak X-ray peak can be attributed to the high-temperature phase β-MnPd, which may also have undergone a phase transformation to β₁-MnPd. It can be calculated that the reflection with the highest intensity of the β- and β₁-phase must in both cases be located at around 40°. However, no further...
peaks of the intergranular phase were distinguished in the XRD spectra of the SHT condition, which hampers clear identification.

For the specimens subjected to aging at 500 °C, peaks related to austenite (γ), epsilon martensite (ε), and also to the evolved precipitates were clearly observable besides bcc diffraction lines (Fig. 3.5). Considering first the formation of γ and ε, it is known from Ni-based maraging steels that during aging treatment partial reversion from martensite (α′) to γ occurs in the α+γ phase region [9, 34]. This type of γ is often referred to as reverted γ, and the formation mechanism is associated with a diffusional process leading to an enrichment of Ni within the reverted γ [34]. The martensite start temperature (Ms) depends strongly on composition, and it decreases with increasing Ni content [35]. Consequently, due to Ni enrichment the reverted γ gets stabilized upon quenching to room temperature (RT). The Fe–Mn system features transformation characteristics similar to those of Fe–Ni alloys [29, 36]. However, in the Fe–Mn system, ε-martensite occurs in the compositional range between 10 and 27 wt.% Mn [36, 37]. Hence it can be concluded for the alloys investigated here that during aging at 500 °C reverted γ enriched in Mn evolves, and upon quenching to RT is partially transformed to ε-martensite. Peaks related to the evolving precipitates can be observed in the XRD patterns of Fe-10Mn-3Pd and Fe-10Mn-6Pd (indicated by stars in Fig. 3.5) after just 30 h of aging, and on further aging for 1200 h they become even more clearly visible. Figure 3.5b,c show enlarged sections of the corresponding angular ranges. For Fe-10Mn-1Pd only a weak peak corresponding to the precipitates is observable (insert 2 in Fig. 3.5b) after 1200 h of aging. APT measurements reveal that the precipitates consist mainly of Mn and Pd and, due to their composition, can be related to the β- or β1-MnPd intermetallic phase. Table 3.2 summarizes the peak positions of the precipitates observed in the XRD patterns of the specimens aged for 1200 h at 500 °C, and also lists the 2θ values for β and β1. The observed reflections of the precipitates only match the β1 phase. Some of the expected reflections of the β1 phase were, however, not revealed, as they either showed an overlap with the α, γ or ε phases or because their relative intensity is very low. The combined results of the APT and XRD measurements confirm that in the Fe–Mn–Pd maraging steels, as also in Fe–Mn-based systems containing Ni or Pt, the precipitates in the over-aged state exhibit an ordered fct structure which corresponds to the intermetallic phase near the equiatomic composition of the respective Mn–X (X = Ni, Pd, Pt) binary phase
Table 3.2. Peak positions (2θ in °) of the precipitates observed in the XRD spectra of specimens aged for 1200 h at 500 °C (Fig. 3.5) and calculated for the fct β₁-MnPd phase with \( a = 0.411 \) nm and \( c = 0.351 \) nm, and for the bcc β-MnPd phase with \( a = 0.315 \) nm. The relative intensities are given in parentheses.

<table>
<thead>
<tr>
<th>System</th>
<th>( a ) (nm)</th>
<th>( c ) (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>0.411</td>
<td>0.351</td>
<td>Present work</td>
</tr>
<tr>
<td>Fe-10Mn-3Pd</td>
<td>0.4069</td>
<td>0.3585</td>
<td>[40]</td>
</tr>
<tr>
<td>Fe-10Mn-6Pd</td>
<td>0.402</td>
<td>0.3660</td>
<td>[39]</td>
</tr>
<tr>
<td>β₁-MnPd</td>
<td>0.401</td>
<td>0.368</td>
<td>[12]</td>
</tr>
<tr>
<td>θ-NiMn</td>
<td>0.369</td>
<td>0.349</td>
<td>[38]</td>
</tr>
<tr>
<td>Fe-9Pt-9Mn (500 h at 500 °C)</td>
<td>0.401</td>
<td>0.368</td>
<td>[12]</td>
</tr>
<tr>
<td>Fe-6Mn-12Ni (1000 h at 450 °C)</td>
<td>0.3734</td>
<td>0.3512</td>
<td>[14]</td>
</tr>
</tbody>
</table>

Table 3.3. Comparison of lattice parameters determined via XRD for the intermetallic particles in the different ternary maraging systems, and those of the fct phase of the respective binary phase diagrams.

<table>
<thead>
<tr>
<th>System</th>
<th>( a ) (nm)</th>
<th>( c ) (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>0.410</td>
<td>0.352</td>
<td>Present work</td>
</tr>
<tr>
<td>Fe-10Mn-6Pd</td>
<td>0.411</td>
<td>0.351</td>
<td>Present work</td>
</tr>
<tr>
<td>β₁-MnPd</td>
<td>0.402</td>
<td>0.3660</td>
<td>[39]</td>
</tr>
</tbody>
</table>

Table 3.3 summarizes the lattice parameters of the precipitates in the different ternary maraging steels, and those of the corresponding intermetallic binary phases. A good agreement is observed and the lattice parameters of the precipitates differ on average by only 1% from the values of the corresponding binary phases.
3.4 Summary

In this study the precipitates which form during aging at 500 °C in Fe–Mn–Pd maraging steels were characterized using atom probe tomography and X-ray diffraction. Alloys containing 1, 3, and 6 wt.% Pd with a fixed Mn content of 10 wt.% were investigated. The steels exhibit considerable hardening upon aging. APT results in combination with XRD measurements reveal that the precipitates in the over-aged state consist mainly of Mn and Pd and can be related to the face-centered tetragonal $\beta_1$-MnPd intermetallic phase, which is similar to what has been observed for Fe–Mn–Ni and Fe–Mn–Pt maraging steels.

Acknowledgements

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References


4 Overall transformation processes

In Chapter 2 and 3 the precipitation reaction of martensitic Fe–Mn–Pd alloys has been described in detail. Besides that in maraging steels it is very important to understand the process associated with the transformation of martensite to austenite (α’→γ). Chapter 4 discusses the mechanisms governing the reverse α’→γ transformation for binary martensitic Fe–Mn steels and the effect of prior precipitation on austenite reversion is studied for ternary Fe–Mn–Pd maraging-type alloys.
Reverse $\alpha' \rightarrow \gamma$ transformation mechanisms of martensitic Fe–Mn and age-hardenable Fe–Mn–Pd alloys upon fast and slow continuous heating\(^1\)

The mechanisms governing the reverse martensite ($\alpha'$) to austenite ($\gamma$) transformation ($\alpha' \rightarrow \gamma$) and the effect of prior precipitation on the austenite reversion are investigated for martensitic Fe–Mn alloys containing 5 and 10 wt.% Mn and their age-hardenable variants with addition of 1 wt.% Pd, respectively. Dilatometric experiments employing heating rates between 0.5 and 200 K/min, atom-probe tomography measurements on continuously heated specimens, and thermo-kinetic simulations were performed. On fast heating (200 K/min), the $\alpha' \rightarrow \gamma$ transformation appeared in a single stage and can be regarded as a partitionless and interface-controlled reaction. In comparison to the binary alloys, the transformation temperatures of the Pd-containing steels are considerably increased, due to precipitates which act as obstacles to migrating austenite/martensite interfaces. For low heating rates of 0.5 and 2 K/min, splitting of the $\alpha' \rightarrow \gamma$ transformation into two consecutive stages is observed for both the binary and the ternary alloys. With the assistance of thermo-kinetic simulations, a consistent description of this phenomenon is obtained. The first transformation stage is associated with the decomposition of the martensite matrix into Mn-rich and Mn-deficient regions, and the austenite formation is dominated by long-range diffusion. In the second stage, the austenite reversion mechanism changes and the Mn-depleted regions transform in a predominantly interface-controlled mode. This is corroborated by the results for the ternary alloys. The precipitates mainly impede the austenite formation in the second stage, which occurs over a considerably wider temperature range compared to the binary alloys.

4.1 Introduction

The superior combination of mechanical properties in maraging steels, such as high strength and good toughness, are commonly achieved via a heat treatment in the two-phase field of ferrite ($\alpha$) and austenite ($\gamma$). During aging, two important reactions occur: (i) The formation of strengthening nanometer-sized intermetallic precipitates in the martensitic ($\alpha'$) matrix; and (ii) partial reversion of martensite to austenite ($\alpha' \rightarrow \gamma$). Both precipitation and the $\alpha' \rightarrow \gamma$ transformation play a major role in maraging steels, as they significantly affect their

mechanical properties [1, 2]. Understanding the phenomena associated with the $\alpha' \rightarrow \gamma$ transformation is also of importance in various advanced high-strength steels, including maraging steels, quenched and partitioned (Q&P) steels, dual-phase (DP) steels, and transformation-induced plasticity (TRIP) steels [3].

Continuous heating dilatometry (DIL) is often employed to study the kinetics of solid-state transformation in steels [4-9], and the length change associated with the phase transformation is measured. In the case of the $\alpha \rightarrow \gamma$ transformation, the dilatometer signal is characterized by a pronounced contraction due to the difference in specific volume of the $\alpha$ and $\gamma$ phases. During a phase transformation, two principal processes may occur: atomic diffusion and interface migration. The heating rate within a dilatometer controls the mechanisms that govern the redistribution of solute atoms, which can vary from long-range diffusion during slow heating to short-range diffusion at moderate heating rates to massive transformation mechanisms at very fast heating rates [9-13]. In binary Fe–Mn alloys (containing ~4-10 wt.% Mn) and Fe–Ni alloys (containing ~10-29 wt.%Ni), a lath martensitic microstructure, similar to the characteristic microstructure of maraging steels, is formed under most cooling conditions [14-16]. Upon heating of such binary martensitic alloys in a dilatometer, the signal associated with the $\alpha' \rightarrow \gamma$ transformation typically indicates a single-stage austenite reversion. At slow heating rates, the dominance of long-range diffusional processes during the $\alpha' \rightarrow \gamma$ transformation has been suggested. However, partitioning of the matrix into solute-rich and solute-depleted regions has not been observed to affect the reverse transformation [17, 18]. In various maraging steels, such as grade 350, Fe–Ni–W, and Fe–Mn–Mo (to name a few), precipitation is known to precede austenite reversion. A peculiarity of the $\alpha' \rightarrow \gamma$ transformation was revealed in such steels: at slow and moderate heating rates, the $\alpha' \rightarrow \gamma$ transformation was seen to split into two stages, whereas fast heating led to a single-stage transformation [9, 10, 17-21]. The splitting behavior is attributed to the partitioning of the matrix into solute-rich and solute-depleted regions. It was suggested that this process is enhanced by a prior precipitation reaction [10, 17]. Accordingly, in contrast to binary alloys, partitioning considerably affects the reverse austenite formation. However, it is not completely clear whether partitioning is sufficient to explain the pronounced splitting behavior of the $\alpha' \rightarrow \gamma$ transformation found in maraging steels.
Only a few investigations into the redistribution of substitutional alloying elements in the course of the \( \alpha^{\prime} \rightarrow \gamma \) transformation of such binary martensitic alloys have been reported in literature. The interplay between precipitation and austenite reversion is also not yet fully understood. By coupling various experimental techniques and applying computational simulation of solid-state transformation, this study aims to fill this gap. We compare transformation mechanisms of binary martensitic Fe-5Mn and Fe-10Mn (in wt.%) and ternary age-hardenable Fe-5Mn-1Pd and Fe-10Mn-1Pd alloys. For Fe-10Mn-1Pd, it was observed that nm-sized particles, rich in Pd and Mn, evolve during isothermal aging at temperatures in the range of 300-500 °C, which gives rise to a significant increase in strength [22]. This indicates that the alloy exhibits all of the characteristic features of maraging steels. The compositions chosen are well-suited for revealing a deeper insight into the mechanisms that govern the \( \alpha^{\prime} \rightarrow \gamma \) transformation with and without prior precipitation, because the matrix compositions of the age-hardened alloys with the addition of only 1 wt.% Pd (equivalent to 0.53 at.%) are very similar to those of their binary counterparts. In this paper, various aspects of the transformation mechanisms, including partitioning of solute atoms, diffusion-controlled versus interface-controlled \( \gamma \)-growth, and precipitate drag, are considered. The model alloys chosen are characterized by DIL using heating rates from 0.5-200 K/min. Atom-probe tomography (APT) measurements performed on continuously heat-treated Fe-10Mn-1Pd samples reveal microstructural relations between Pd/Mn-rich precipitates, martensitic matrix and reverted austenite. Thermo-kinetic simulations in the binary Fe–Mn system using the solid-state transformation software MatCalc contribute to the theoretical understanding of the transformation mechanisms.

### 4.2 Experimental procedure

Alloys of the nominal compositions Fe-5Mn, Fe-5Mn-1Pd, Fe-10Mn, and Fe-10Mn-1Pd were prepared by melting the elemental ingredient materials (Fe: Armco; Mn: 99.9% pure, Alfa Aesar, Germany; Pd: 99.95% pure, UBS, Switzerland) in a vacuum induction furnace under 300 mbar argon atmosphere (99.998% purity) and subsequent casting into copper molds. The ingots were then sealed in quartz tubes under 215 mbar argon atmosphere, solution-heat-treated (SHT) for 12 h at 1250 °C to ensure a homogenous distribution of the elements, and then quenched in water to room temperature (RT).

To track the aging response of the alloys investigated, hardness measurements (Vickers hardness, HV10) were performed on specimens isothermally heat-treated at 500 °C for up to 1800 min. The
measurements were carried out using a Brickers 220 hardness tester (Gnehm, Switzerland). Five measurements with an indentation time of 6 s were taken per specimen. The relative change in specimen length $\Delta L/L_0$ with temperature, where $L_0$ is the initial length at RT, was measured using a DIL805 dilatometer (Baehr, Germany). The cylindrical specimens had a diameter of 5 mm and an initial length of 10 mm, and were kept between quartz tubes within the dilatometer. The temperature was measured by means of a chromel-alumel thermocouple spot-welded to the specimens in a central location. The specimens were heated up to 1100 °C with a heating rate that was varied between 0.5 and 200 K/min. All measurements were conducted under vacuum ($<10^{-2}$ mbar) to minimize oxidation of the specimens.

APT analysis was performed on two DIL specimens continuously heated within the dilatometer at a rate of 20 K/min to 600 °C or 705 °C, respectively, held at that temperature for one second, and subsequently quenched to RT at a rate of 200 K/min. For the APT experiments bars of $0.3 \times 0.3 \times 7$ mm$^3$ in size were cut from the DIL samples. To obtain the needle-like specimen shape required for APT, the bars were electrochemically polished in a standard two-step procedure [23], using a solution of 10 vol.% perchloric acid and 90 vol.% methanol, followed by polishing in a solution of 2 vol.% perchloric acid and 98 vol.% butoxyethanol. The APT experiments were performed on a LEAP™ 4000X HR (Cameca) unit in laser mode (wavelength 355 nm) using a specimen temperature of ~24 K, at a pulse frequency of 250 kHz and a detection rate of 1%. The laser energy was adjusted between 100 and 150 pJ, ensuring that field evaporation conditions were comparable among the samples. Data processing was performed using the IVAS 3.6.6 software package (Cameca) [24]. The isoconcentration surface method [25, 26] was used to identify and characterize microstructural inhomogeneities such as nm-size precipitates or interfaces.

### 4.3 Thermo-kinetic simulation

For the thermo-kinetic simulation of the $\alpha' \rightarrow \gamma$ transformation in Fe–Mn, the solid-state transformation software MatCalc [27] was used. MatCalc takes into account CALPHAD-assessed thermodynamic model parameters (thermodynamic database mc_fe_v2.015.tdb) for the evaluation of chemical potentials, driving forces and interfacial energies between matrix and precipitate. The latter is based on the generalized broken-bond model [28] and takes into account curvature (size) [29] as well as diffuse interface effects [30]. The diffusion data needed for the evaluation of the precipitate and austenite growth kinetics based on the SFFK model [31, 32] is taken from the mobility database mc_fe_v2.002.ddb. The rate of radius and chemical composition change of each precipitate is evaluated by applying the thermodynamic extremum principle [33-35]. To determine the evolution of the entire
precipitate population, the rate equations are integrated numerically under the constraint of mass conservation. Time integration of the evolution equations is carried out according to the numerical Kampmann-Wagner approach [36]. This evaluation routine delivers the evolution of size distributions, mean radii, and phase fractions of precipitates during arbitrary heat treatments. Further details of the models used and the numerical treatment of the evolution equations were presented by Svoboda et al. [31] and Kozeschnik et al. [37]. For the simulations, the quenched martensitic matrix ($\alpha'$) is assumed to have the same thermodynamic properties as the ferritic counterpart ($\alpha$) with an increased density of dislocations ($10^{15}/m^2$ compared to $10^{12}/m^2$ in ferrite) [38]. Heterogeneous nucleation of austenite is allowed at martensitic lath boundaries in line with microstructural evidence [13, 39].

4.4 Results

4.4.1 Isothermal aging

Figure 4.1 displays the isothermal age-hardening curves of the four alloys at 500 °C. Both alloys doped with 1 wt.% Pd significantly strengthen upon aging. The hardness data confirm that both Pd-containing steels exhibit a typical maraging behavior [2, 22], i.e. the hardness values rapidly increase until the peak hardness is reached, followed by a slow gradual decrease with subsequent aging time. It is seen that the time required to reach peak

\[ T_{\text{aging}} = 500 \degree C \]

\[ 
\begin{align*}
\text{Fe-10Mn-1Pd} & \quad \text{Fe-5Mn-1Pd} \\
\text{Fe-10Mn} & \quad \text{Fe-5Mn}
\end{align*}
\]

\[ 
\begin{align*}
\text{HV 10} & \quad \text{SHT} \quad \text{Time (min)}
\end{align*}
\]
hardness for the alloy Fe-5Mn-1Pd is considerably longer than for Fe-10Mn-1Pd. By contrast, the hardness of the binary analogs of these alloys decreases monotonically for the aging times used in the experiments.

4.4.2 Continuous heating dilatometry

Figure 4.2 displays the relative length change with temperature of the alloys investigated at a heating rate of 20 K/min. According to Ref. [20], the dilatometer curves can be subdivided into the following three main stages: (a\(^\alpha\)) aging of martensitic matrix; (r) reverse \(\alpha' \rightarrow \gamma\) transformation (contraction); and (a\(^\gamma\)) aging and homogenization of reversed austenite.

In the binary alloys for heating at 20 K/min, \(\alpha'\) transforms to \(\gamma\) in a single step. The austenite start (\(A_s\)) and finish (\(A_f\)) temperatures were determined as the temperatures at which the relative change of length as a function of temperature deviates from linearity by a set value of 2 %. Table 4.1 lists the characteristic temperatures extracted from the continuous heating experiments at a rate of 20 K/min. For the alloys Fe-5Mn-1Pd and Fe-10Mn-1Pd, the reverse \(\alpha' \rightarrow \gamma\) transformation starts at a temperature about 30 °C higher than for their Pd-free counterparts (Table 4.1). For the Pd-containing alloys, the reverse transformation splits up
into two sub-stages (r.1 and r.2), where sub-stage r.2 exhibits a much smaller magnitude of contraction than sub-stage r.1 (Fig. 4.2).

**Table 4.1.** Start temperature ($A_s$), and end temperature ($A_f$) of the reverse $\alpha' \rightarrow \gamma$ transformation in the alloys investigated, as determined by DIL (20 K/min).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$A_s$ (°C)</th>
<th>$A_f$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-5Mn</td>
<td>682</td>
<td>765</td>
</tr>
<tr>
<td>Fe-5Mn-1Pd</td>
<td>713</td>
<td>857</td>
</tr>
<tr>
<td>Fe-10Mn</td>
<td>597</td>
<td>646</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>633</td>
<td>815</td>
</tr>
</tbody>
</table>

Figure 4.3 presents dilatation curves, $\Delta L/L_0$ vs. temperature, measured at different heating rates (0.5-200 K/min), along with the corresponding derivatives of $\Delta L/L_0$ with respect to temperature for Fe-10Mn (a,b) and Fe-10Mn-1Pd (c,d). At the heating rates of 200 K/min, the $\alpha' \rightarrow \gamma$ transformation appears in a single stage, while for very low heating rates (0.5 and 2 K/min) a splitting of the reverse transformation is visible. At 20 K/min, splitting is only observed for the Pd-containing alloy.
and 20 K/min, the reverse transformation of the binary alloy proceeds in a single step, which is recorded as a sharp drop in specimen length (Fig. 4.3a). This effect is also reflected in a pronounced (negative) single peak in the differentiated curve (Fig. 4.3b). In contrast, at heating rates of 2 and 0.5 K/min, \( \alpha' \rightarrow \gamma \) splits up into two distinct stages, which is particularly obvious for the slowest heating rate of 0.5 K/min, and the contraction associated with the reverse transformation becomes less steep. This splitting is also revealed clearly by the occurrence of two peaks in the differentiated curves (insert in Fig. 4.3b). For the Pd-containing alloy Fe-10Mn-1Pd (Fig. 4.3 c,d), splitting is observed for the heating rates from 0.5 K/min to 20 K/min. Only at the fastest heating of 200 K/min does \( \alpha' \rightarrow \gamma \) proceed in a single step.

### 4.4.3 Thermo-kinetic simulations

Figure 4.4 presents the results of the thermo-kinetic simulation for Fe-10Mn at heating rates of 200 K/min and 0.5 K/min, corresponding to the fastest and slowest heating rates employed in the DIL measurements. At both heating rates, nucleation starts below 430 °C and the \( \gamma \)-nuclei density \( N_{d}^{\gamma} \) was found to be constant for an austenite volume fraction \( f_{\gamma} \) above \( \sim 3 \times 10^{-4} \text{ vol.}\% \) (Fig. 4.4). Accordingly, the \( \alpha' \rightarrow \gamma \) transformation proceeds mainly within the \( \gamma \)-growth regime. The onset of nucleation is defined as the temperature where the \( \gamma \)-nuclei size becomes larger than the unit cell dimension of \( \gamma \). The temperature where the evaluated \( N_{d}^{\gamma} \) remains constant with increasing temperature (start of growth regime) is also marked in Fig. 4.4.

Upon fast heating (200 K/min), our simulation predicts single-stage austenite formation, which is also reflected by a single peak in the transformation rate \( (df_{\gamma}/dT, \text{Fig. 4.4a}) \). For \( f_{\gamma} \geq 2 \text{ vol.}\% \), which corresponds approximately to the experimentally accessible start of austenite formation, the evolving \( \gamma \) has a composition similar to that of the parent \( \alpha' \)-phase.

Upon slow heating (0.5 K/min), splitting of the \( \alpha' \rightarrow \gamma \) transformation is predicted and two peaks are observed in the transformation rate curve (Fig. 4.4b). Since the present modeling approach is most accurate at low phase fractions of the transformed phase and becomes increasingly inaccurate at higher phase fractions, the final stages of transformation are designated by a black dotted line. A high Mn concentration in \( \gamma \) \( C_{Mn}^{\gamma} \) is observed at the incipient stage of the reverse transformation (550 °C). With increasing temperature, \( C_{Mn}^{\gamma} \)
Fig. 4.4. Results from thermo-kinetic simulation of Fe-10Mn for the heating rates (a) 200 K/min and (b) 0.5 K/min. The Mn-contents in $\alpha'$ ($C_{\text{Mn}}^{\alpha'}$) and $\gamma$ ($C_{\text{Mn}}^{\gamma}$), the volume fraction of $\gamma$ ($f_\gamma$), and the transformation rate ($df_\gamma/dT$) as a function of temperature are displayed. The start temperature of nucleation and the temperature where the evaluated nucleation density ($N_{\text{eff}}^f$) was observed to be constant (start of growth regime) are marked. Upon fast heating (200 K/min) a single stage austenite formation is predicted and $C_{\text{Mn}}^{\gamma}$ is similar to that of the parent $\alpha'$-phase. At slow heating rates (0.5 K/min) a splitting of the $\alpha'$--$\gamma$ transformation is apparent along with concentration changes in $\alpha'$ and $\gamma$.

The Mn-content in $\alpha'$ ($C_{\text{Mn}}^{\alpha'}$) declines considerably, from initially ~10 at.% to ~4 at.% during the first step of austenite reversion. In contrast, it changes only slightly in the second step.
4.4.4 Atom-probe tomography

For the APT measurements of Fe-10Mn-1Pd, two different microstructural regimes regarding the reverse transformation state (see Fig. 4.2) were chosen: (i) interrupting continuous heating at 600°C before the onset of transformation and (ii) interrupting at 705 °C, at the peak of transformation stage r.1 (Fig. 4.2 and Fig. 4.3d). In both cases, the specimens were subsequently quenched to RT at a cooling rate of 200 K/min.

Figure 4.5 presents three-dimensional reconstructions of the Fe-10Mn-1Pd specimen heated to 600 °C. The Pd atoms and the isoconcentration surfaces for Pd (blue) and Mn (red) corresponding to concentration threshold values of 5 at.% and 22 at.%, respectively, are displayed. As seen in Fig. 4.5, precipitation occurred in this heat-treated state and the particles are clearly enriched in Pd and Mn. Based on the isoconcentration value of 5 at.% Pd, the volume-equivalent precipitate radius, $r_{equ}$, as determined by assuming a spherical shape of precipitates, amounts to $2.6\pm0.8$ nm with a volume fraction of the precipitates ($V_p$).

Table 4.2. Composition of the DIL specimen heated to 600 °C (Fig. 4.5) of the entire reconstructed data set (overall) and without the Pd/Mn-rich precipitates (matrix).

<table>
<thead>
<tr>
<th></th>
<th>Fe (at.%  )</th>
<th>Mn (at.%  )</th>
<th>Pd (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>88.81 ± 0.03</td>
<td>10.64 ± 0.01</td>
<td>0.556 ± 0.002</td>
</tr>
<tr>
<td>Matrix</td>
<td>89.75 ± 0.03</td>
<td>10.05 ± 0.01</td>
<td>0.206 ± 0.001</td>
</tr>
</tbody>
</table>

Error is estimated from the number of atoms in the analysis [23]
of ~2 %. Because the precipitate size and the volume fraction are sensitive to the choice of the isoconcentration threshold value, the calculated values are considered to deliver qualitative tendencies of the microstructural changes occurring during heat treatment and are thus only indicative. To evaluate the reduction in the Mn-content of the martensitic matrix due to precipitation, Table 4.2 lists the overall and matrix content of the main constituents of the data displayed in Fig 4.5. To obtain the composition of the matrix the Pd/Mn-rich precipitates were cut out of the reconstructed data set using Pd isoconcentration surfaces. The Mn-content of the matrix is reduced by about 0.6 at.% compared to the overall composition.

**Fig. 4.6.** APT analysis of a dilatometric sample of Fe-10Mn-1Pd heated to 705 °C (heating rate: 20 K/min). (a) Atom maps of Pd (blue) and Pd isoconcentration surfaces of 5 at.% reveal the occurrence of precipitates; a 6 at.% isoconcentration surface of Mn (red) is used to indicate the distinct phase boundary between Mn-enriched and Mn-depleted regions (box size: 61 × 63 × 250 nm³). (b) Proxigram analysis (bin width 0.3 nm) of the boundary. Results for Fe, Mn (left y-axis) and Pd (right y-axis) are shown and the arrows mark the nominal compositions of the alloy. The black lines indicate the data points used to evaluate the composition at the various sites. The insert shows a Mn atom map for the same view of the data as depicted in (a), and the Mn isoconcentration surface (6 at.%) used for the proxigram analysis is displayed. The black arrow indicates the direction along which the data in the proxigram were taken.
Figure 4.6 presents APT data of the DIL sample heated to 705 °C. The red isoconcentration surfaces for Mn in Fig. 4.6a (set to a concentration value of 6 at.%) indicate a boundary which separates regions enriched in Mn from those depleted in Mn. Pd/Mn-rich precipitates decorating this boundary can be identified. The volume-equivalent radius of these precipitates, $r_{\text{eq}}$, based on the isoconcentration value of 5 at.% Pd was found to be 10±4 nm. To assess the concentration profile across the grain boundary, the proxigram analysis method was used [26]. Prior to the analysis the precipitates were therefore cut out of the reconstructed volume using Pd isoconcentration surfaces.

Figure 4.6b displays the results of the proxigram analysis for Fe, Mn and Pd based on the Mn isoconcentration surfaces of 6 at.% (see also insert in Fig 4.6b). Obviously, we succeeded in capturing a region with a sharp change in Fe and Mn concentration. This sharp change suggests the existence of a pronounced interface and, hence, of diffusional partitioning in the matrix. As $A_s$ increases with decreasing Mn-content, it can be assumed that the Mn-rich region has already transformed to austenite, while the Mn-depleted region has not. Within the martensitic area, the Mn-content has dropped considerably below the nominal composition and appears there to be relatively constant. In the austenitic region, a gradient in the Mn concentration, which runs into a plateau value of around 12.2 at.% Mn further away from the interface, can be recognized.

4.5 Discussion

4.5.1 Precipitation reaction

The strengthening of the Pd-containing alloys seen in the isothermal hardening curves (Fig. 4.1) can be attributed to the evolution of Pd/Mn-rich precipitates forming within the martensitic matrix during aging [22]. The shifted peak hardness of Fe-5Mn-1Pd compared to Fe-10Mn-1Pd reflects that Mn participates in the precipitation process and, hence, its overall content strongly affects the aging kinetics. The gradual hardness drop of the Fe–Mn alloys can be attributed to thermally-induced recovery of the lath martensite and the formation of reverted austenite [40].

Regarding dilatometric investigations, it is known from 18 wt.% Ni maraging steels (e.g. grade 350) [9, 10, 19, 41] that precipitation, which was seen to precede the $\alpha' \rightarrow \gamma$ transformation, results in a macroscopic change in specimen dimensions. Even though the formation of Pd/Mn-rich particles prior to the $\alpha' \rightarrow \gamma$ transformation was clearly revealed by
the APT measurements (Fig. 4.5), precipitation is not reflected in the DIL curves. While the lattice constants of the precipitates, which evolve during continuous heating, have not yet been determined, the DIL experiments indicate that the lattice mismatch between the precipitates and the martensitic matrix is rather low. The fact that precipitation is not observable in a DIL experiment is not unusual. In investigations of simple ternary maraging steels such as Fe–Ni–Mo, Fe–Mn–Mo or Fe–Ni–W [18, 20], which age-harden due to the formation of Fe/Mo- or Fe/W-rich precipitates, no precipitation reaction was revealed by means of dilatometry either.

4.5.2 Reverse $\alpha' \rightarrow \gamma$ transformation

The initial state in all DIL measurements was $\alpha'$-martensite, which formed during quenching of the SHT high-temperature austenite phase to room temperature. Therefore, at RT the alloys are in a non-equilibrium condition. In the subsequent heat-treatment, the heating rate and, hence, the time available for diffusion have a significant influence on the progression of the $\alpha' \rightarrow \gamma$ transformation. For both Fe-10Mn and Fe-10Mn-1Pd under fast heating (200 K/min), the reverse transformation is characterized by a single stage, while under very slow heating (0.5 K/min) it splits up into two stages (Fig. 4.7a). In the following, the two cases (i) fast heating (200 K/min) and (ii) slow heating (0.5 K/min) are discussed separately. To understand the role of Mn redistribution in the reverse transformation of the binary Fe-10Mn alloy, the experimental results are compared with thermo-kinetic simulations. It will be shown that (i) on fast heating, the formation of austenite proceeds in an interface-dominated manner and (ii) on slow heating, austenite reversion takes place in a dual-step process, where diffusional mechanisms dominate the first stage and the second stage is controlled by interface migration. By comparing the results for the binary alloys with the Pd-containing alloys which exhibit precipitation, the interplay between the precipitates and the reverse transformation can be evaluated. It will be demonstrated that the precipitates mainly retard $\gamma$-growth when austenite is formed in an interface-controlled manner.

4.5.2.1 Reverse $\alpha' \rightarrow \gamma$ transformation on fast heating (200 K/min)

The bulk diffusion rate of substitutional elements, such as Ni or Mn, in binary Fe-based alloys is very low [7, 42] and is assessed using the mobility database mc_fe_v2.002.ddb. It is generally considered that, on fast heating or cooling, the $\alpha \rightarrow \gamma$ or $\gamma \rightarrow \alpha$ transformation
proceeds without partitioning (long-range diffusion) of substitutional solutes and can be regarded as compositionally invariant [7, 42]. During a solid-state phase reaction, in principle, nucleation and growth of the product phase into the parent phase occur. Liu et al. [7] investigated the $\alpha \rightarrow \gamma$ transformation of an Fe-2.96 at.% Ni alloy upon fast heating (50 K/min). They argued that nucleation of $\gamma$ is completed (site saturation) at the start of $\gamma$-growth. They considered the $\alpha \rightarrow \gamma$ transformation upon fast heating as a typical example of a partitionless and interface-controlled reaction.

In Fig. 4.7b, the experimental volume fraction of $\gamma$ in Fe-10Mn (calculated from the DIL curves using the lever rule [42]) and the simulated $f_{\gamma}$ are compared as a function of temperature at a heating rate of 200 K/min. The simulated trend agrees well with the experimental results. As indied in Fig. 4.4a (start of growth regime) the number density of $\gamma$-nuclei ($N_{\alpha}^{\gamma}$) is constant above ~612°C. This suggests that nucleation is completed at the beginning of the $\alpha' \rightarrow \gamma$ transformation. It was further revealed that the evolving $\gamma$ had a composition close to that of the parent $\alpha'$-phase during fast heating. Consequently, and in accordance with Ref. [7], site saturation at the onset of $\gamma$-growth prevails, the occurrence of diffusional processes can be neglected, and the free energy change associated with the phase transformation is dissipated mainly by migration of the $\alpha'/\gamma$ interfaces.

For the ternary alloy Fe-10Mn-1Pd, single-stage austenite formation upon fast heating (Fig. 4.7a) also indicates that for this alloy the reverse transformation occurs without partitioning of the matrix. Interestingly, comparing the dilatometer curves of Fe-10Mn and Fe-10Mn-1Pd, the $\alpha' \rightarrow \gamma$ transformation shifts to considerably higher temperatures, which indicates a strong retarding effect of the Pd/Mn-rich precipitates on the transformation kinetics. Taking the temperature at the maximum rate of change in length ($A_M$, see insert in Fig. 4.7a) as a reference point, the reverse transformation of Fe-10Mn-1Pd is shifted by about 87 °C to higher temperatures compared to the binary Fe-10Mn alloy. Higher transformation temperatures in turn indicate that a greater driving force (dF) is required to accomplish the phase transformation. In the case of a partitionless transformation, dF is given by the difference of the Gibbs free energy of the product phase ($\gamma$) and the parent phase ($\alpha'$) [43].

In Fig. 4.7c, the driving force for the partitionless $\alpha' \rightarrow \gamma$ transformation in Fe-10Mn is displayed as a function of temperature; $T_0$ denotes the temperature at which the Gibbs free
Fig. 4.7. (a) Measured dilatation curves for Fe-10Mn and Fe-10Mn-1Pd for heating rates of 200 K/min and 0.5 K/min. The inserts display the corresponding differentiated dilatation curves. $A_M$ is the temperature at the maximum rate of change in length and $\Delta A_M$ describes the difference between the binary and ternary alloy. (b) Simulated volume fraction of $\gamma$ as a function of temperature at the fastest (200 K/min) and slowest (0.5 K/min) heating rates compared with experimental results. The inserts show the transformation rate ($df_\gamma/dT$) as a function of temperature for the corresponding heating rates. (c) Driving force for the $\alpha' \rightarrow \gamma$ transformation with and without partitioning. At the temperature $T_0$, the Gibbs free energy of $\alpha'$ equals that of $\gamma$. Below $T_0$, growth of $\gamma$ can only occur through a diffusion-dominated process. Above $T_0$, a mixed mode (diffusion- and interface-dominated) can be expected, at which on fast heating diffusional processes are negligible and interface-dominated austenite growth occurs.
energy of both phases is the same. Based on Fig. 4.7c, the increase in the transition temperatures of Fe-10Mn-1Pd ($\Delta A_m$) can be converted into an increase in $dF$ necessary to accomplish the transformation. Using $A_m$ as a reference point, $dF$ for Fe-10Mn-1Pd is higher by about 100 J/mol compared to $dF$ for Fe-10Mn. Precipitates can effectively retard the migration of grain boundaries. Hence, it is suggested here that the estimated extra driving force of 100 J/mol for Fe-10Mn-1Pd (or, equivalently, the increased transformation temperature) is required to overcome the counteracting pinning pressure ($p_{\text{pin}}$) exerted by the precipitates on the migrating $\gamma/\alpha'$ interfaces during austenite reversion. In Ref. [22], it was reported that, for isothermally heat-treated samples, the evolving Pd/Mn precipitates are coherent with the matrix up to the peak-aged condition and at least semi-coherent in the overaged state. For the extreme case of incoherent precipitates, the pinning pressure can be calculated using the Zener equation [44],

$$p_{\text{pin}}^{\text{incoherent}} = \frac{3}{2} \left( \frac{V_p \mu}{r} \right)$$  \hspace{1cm} (4.1)

where $V_p$ is the volume fraction of the precipitates, $\mu$ is the interfacial energy per unit area, and $r$ is the precipitate radius. For the other extreme case of coherent particles (assuming that the bypassing interphase boundary makes the precipitates incoherent), the pinning energy can be calculated [44] as

$$p_{\text{pin}}^{\text{coherent}} = 6 \left( \frac{V_p \mu}{r} \right).$$ \hspace{1cm} (4.2)

With $r \approx 2.6$ nm, $V_p \approx 2\%$ (adopted from the APT measurement, Fig. 4.5), and setting $\mu \approx 0.6$ J/m$^2$ [45], the pinning pressure for incoherent precipitates is estimated to be 7 MPa and for coherent precipitates to be 28 MPa. This corresponds, respectively, to pinning energies of around 49 J/mol and 196 J/mol (converted by using the specific volume of 7.09 cm$^3$/mol for pure Fe). Consequently, the back pressure from the precipitates can be sufficient to retard the reverse martensite-to-austenite transformation of the Pd-containing alloys, shifting it to considerably higher temperatures.

The transformation temperatures of the binary Fe–Mn alloy depend strongly on the Mn-content [14]. Accordingly, one might argue here that the formation of Pd/Mn-rich precipitates results in a reduced Mn-content in the $\alpha'$-matrix and thus in an increase of the transformation temperature. The APT analysis of the specimen heated to 600°C (Fig. 4.5), i.e. prior to the start of the austenite reversion, revealed, however, that the matrix Mn-
content is reduced by about only 0.6 at.% compared to the overall Mn-content of the entire reconstructed data set (Table 4.2). Taking the DIL results of Fe-5Mn and Fe-10Mn into account, such a reduction in Mn concentration may correspond to an $A_M$-shift of only about 13 °C.

### 4.5.2.2 Reverse $\alpha' \rightarrow \gamma$ transformation on slow heating (0.5 K/min)

In contrast to fast heating, the $\alpha' \rightarrow \gamma$ transformation splits up into two sub-stages under slow heating for both Fe-10Mn and Fe-10Mn-1Pd. Literature on the behavior of binary ferrous alloys (Fe–Mn or Fe–Ni) with a lath-type martensite microstructure at slow heating rates is rather scarce. To the authors’ knowledge, splitting of the reverse austenite formation for such binary martensitic alloys has not been reported, but it has been observed for various maraging steels [9, 10, 17-21]. In Refs. [18, 20], the ternary model alloys Fe–Ni–W, Fe–Ni–Mo, and Fe–Mn–Mo were investigated. These alloys harden during continuous heating due to the formation of Fe/W- and Fe/Mo-rich particles. The splitting of the $\alpha' \rightarrow \gamma$ transformation in Refs. [18, 20] was explained in terms of partitioning of the alloy into zones enriched and depleted in Ni (or Mn) promoted by precipitation during heating. Because in the Fe–Ni system, $A_s$ is raised as the Ni concentration decreases, in a fashion similar to the behavior of the Fe–Mn system upon a decrease of Mn concentration, the zones enriched in Ni start to transform at temperatures which are lower than for the zones deficient in Ni. In consequence, a two-stage behavior of the dilatometer curve results. Kapoor et al. [9, 10], who investigated a 18 wt.% Ni maraging steel (350-grade), also observed a two-step behavior of the $\alpha' \rightarrow \gamma$ transformation at heating rates below 33.6 K/min. They concluded that the first step is associated with long-range diffusion and the second step presumably with a shear mechanism.

In Fig. 4.7b, the experimental and simulated volume fractions of $\gamma$ in Fe-10Mn as a function of temperature are also compared for a heating rate of 0.5 K/min. Qualitatively, good agreement between theory and experiment is observed. Based on the simulation results, a constant number density of $\gamma$-nuclei ($N_{\gamma}^0$) was evaluated above ~495 °C (Fig. 4.4b) and hence nucleation of $\gamma$ is completed well before the experimentally determined onset of austenite reversion (~540 °C, Fig. 4.7b). Accordingly, we conclude that the $\alpha' \rightarrow \gamma$ transformation proceeds mainly within the $\gamma$-growth regime. In principle, for the growth of a new phase, two limiting cases can be distinguished: (i) diffusion-controlled growth and (ii) interface-
controlled (partitionless) growth. Accordingly, the free energy change between the initial and the evolved states will dissipate either by diffusional processes or by the migration of the interface. The driving forces for both limiting cases plotted in Fig. 4.7c show opposing trends with increasing temperature. Below $T_0$, the driving force for a partitionless reaction is negative and growth of $\gamma$ can only occur through partitioning of the material, i.e. via a diffusion-dominated process. As discussed in the previous section, under fast heating conditions partitioning is negligible and the reverse transformation proceeds in a partitionless interface-dominated manner. Upon heating above $T_0$ and, provided that there is sufficient time for diffusion, a mixed mode control for the austenite growth is expected and, accordingly, the heating rate (time available for diffusion) and the driving forces at a given temperature will determine the amount of energy dissipated in each of the processes.

At the lowest heating rate of 0.5 K/min, the $\alpha+\gamma$ phase field is passed under quasi-equilibrium conditions. Enough time is thus available for long-range diffusion, contributing to the process of energy dissipation. The experimentally observed onset of austenite formation appears at $\sim 540$ °C (Fig. 4.7b), which is in the vicinity of $T_0$, where $dF$ for the partitionless movement of the $\gamma$-boundary is nearly zero. Hence, $\gamma$-growth at the beginning of the first step in the $\alpha' \rightarrow \gamma$ transformation is controlled by Mn-diffusion. Consequently, the alloy is partitioned into regions depleted and enriched in Mn compared to the initial composition. The enriched regions represent the austenite phase, while martensite regions are poor in Mn. In the simulation, large concentration changes in the incipient stage of austenite formation are obtained (Fig. 4.4b). In other words, a large compositional difference between the austenite and martensite matrix associated with the diffusion-controlled growth mechanism indicates that the entropy production rate (dissipation of energy) is at its maximum under these conditions.

At full-equilibrium conditions, where practically “infinite” time for diffusion would be available, the reverse transformation must be completed at $T_{eq}^{\alpha+\gamma \rightarrow \gamma'} = 650$ °C (equilibrium temperature of the phase boundary between the two-phase field $\alpha+\gamma$ and the $\gamma$-phase field for an alloy containing 10 wt.% Mn). However, the experimental and simulated $\gamma$-volume fractions (Fig. 4.7b) show that this is not the case under continuous heating even at a low heating rate. At 650 °C, i.e. at the end of the first stage of the $\alpha' \rightarrow \gamma$ transformation, the increase in austenite volume fraction almost ceases to increase when a level of $f_\gamma = 57$ vol.% is reached. This can be understood by assuming diffusion-dominated austenite growth and
considering the magnitude of the driving force for diffusion-controlled structural changes. With increasing temperature, the driving force for partitioning decreases, but the mobility of the atoms, i.e. the diffusivity, increases. As a result of these two counteracting mechanisms, there exists a certain temperature at which the transformation rate is at maximum. This is reflected by the first peak in the transformation rate observed in the experiments and the simulations (insert in Fig. 4.7b). From these simulations, we can also deduce that during the first step of the reverse transformation the Mn-content of martensite drops considerably (Fig. 4.4b), from initially ~10 at.% to ~4 at.% at low heating rates. Hence a high concentration change occurs along with the evolving austenite, which in turn implies diffusion-dominated growth.

In the beginning of the second step of the $\alpha' \rightarrow \gamma$ transformation, approximately 57% of the material has already transformed and regions depleted in Mn are present. These will start to transform at a higher $A_s$ temperature. This gives rise to a second peak in the experimental and simulated transformation rates (insert of Fig. 4.7b), which has a larger magnitude and extends over a smaller temperature range than the first peak. This indicates a change in the austenite reversion mechanism. From an equilibrium point of view, the alloy Fe-10Mn will enter the single-phase austenite field at above 650 °C. Still, the free energy for the accomplishment of the reverse transformation must be dissipated. With increasing temperature the driving force for a partitionless reaction increases. Accordingly, with increasing temperature the entropy production rate of the system is maximized, with dissipation of energy through progression of the $\gamma$ boundaries into the remaining martensite areas (without the necessity for long-range diffusion). Consequently, and in contrast to the first stage, the residual Mn-deficient martensite areas transform to austenite in an interface-dominated manner in the second stage of the $\alpha' \rightarrow \gamma$ transformation. This conclusion is clearly supported by the simulation.

The two-stage character of the experimental dilatometer curves of the Pd-containing alloy (exhibiting precipitation) also indicates a change in the mechanism of austenite formation upon slow heating (0.5 K/min) compared to the Pd-free alloy. At the first stage of the $\alpha' \rightarrow \gamma$ transformation, $A_s$ is nearly the same for both alloys (Fig. 4.7a). In the extreme case of a diffusion-controlled reaction, the product/parent interface will migrate with simultaneous long-range diffusion of Mn. Consequently, the precipitates do not exert a strong impeding effect on the austenite growth. Upon the further progress of heating, austenite formation in
the Pd-containing alloy nearly comes to a halt in the vicinity of 650 °C, similar to Fe-10Mn. This is due to significant partitioning of the matrix into Mn-rich and Mn-deficient regions below 650 °C, which also takes place in Fe-10Mn-1Pd. For a DIL sample heated within stage r.1 (Fig. 4.6), APT measurements clearly reveal partitioning of the matrix and precipitates located at the $\alpha'/\gamma$ phase boundary. However, compared to Fe-10Mn, the second stage of the $\alpha'\rightarrow\gamma$ transformation is considerably stretched over a wider temperature range for the Pd-containing alloy (Fig. 4.7a). As suggested above for the binary alloy, the reverse transformation in the second step proceeds in an interface-dominated manner, and precipitates are able to effectively impede the migration of the interfaces.

### 4.6 Conclusions

This study provides a consistent picture of the mechanism governing the $\alpha'\rightarrow\gamma$ transformation under fast and slow continuous heating for binary martensitic Fe–Mn alloys containing 5 and 10 wt.% Mn. The results of age-hardenable ternary modifications with the addition of 1 wt.% Pd revealed the effect of prior precipitation on the austenite reversion. Predictions from thermo-kinetic solid-state simulations of the binary alloys very well reproduced the dilatometer results of the $\alpha'\rightarrow\gamma$ transformation. The heating rate was observed to be a significant factor in controlling the time available for the redistribution of Mn. For both fast and slow heating rates, the $\alpha'\rightarrow\gamma$ transformation proceeds within the austenite-growth regime. Upon fast heating, diffusional processes can be neglected and the austenite reversion can be considered as a partitionless and interface-controlled reaction, which appears in a single stage. In contrast, upon slow heating, splitting of the $\alpha'\rightarrow\gamma$ transformation into two consecutive stages was observed. During the first stage, the martensitic matrix partitions into regions enriched and depleted in Mn and the austenite formation is dominated by long-range diffusion. In the second stage, however, the austenite reversion mechanism changes and the residual Mn-depleted regions transform via a predominantly interface-controlled mechanism.

Atom-probe tomography and isothermal hardening tests of age-hardenable Fe–Mn–Pd alloys provided insights into the phase changes and microstructure evolution under continuous heating. Precipitation of Pd/Mn-rich particles was observed prior to the $\alpha'\rightarrow\gamma$ transformation, and partitioning of the matrix in Mn-enriched and Mn-depleted regions was clearly revealed at intermediate stages of the austenite reversion. It was established that the
main effect of precipitation is the retardation of austenite growth, particularly when austenite is formed in an interface-controlled mode. This is reflected in the considerably increased transformation temperatures of the Pd-containing steels on fast heating and a significant broadening of the second stage of the reverse transformation on slow heating. These results contribute to an understanding of the kinetics of the reverse $\alpha' \rightarrow \gamma$ transformation in Fe–Mn and maraging-type alloys, among which Fe–Mn–Pd was chosen as a possible model alloy. They also provide a tool for controlling the transformation through an appropriate choice of heat-treatment conditions.

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References


Martensitic Fe–Mn-based steels are known to suffer from severe embrittlement, when aged at temperature between 300 to 500 °C. This is, however, exactly the temperature range where precipitation hardening is induced. Chapter 5 presents the mechanical performance of binary Fe–Mn (Fe-10Mn) and ternary Fe–Mn–Pd (Fe-10Mn-1Pd) alloys as a function of isothermal aging at 500 °C. A special focus is given on the change of the local chemistry of the prior austenite grain boundaries.
**Atomic-scale characterization of prior austenite grain boundaries in Fe–Mn-based maraging steel using site-specific atom-probe tomography**

The embrittlement and de-embrittlement behavior of an Fe-10Mn-1Pd (in wt.%) maraging steel upon isothermal aging at 500 °C was related to microstructural changes at prior austenite grain boundaries (PAGBs). Site-specific atom probe tomography measurements were performed to analyze the local chemistry of the PAGBs. Tensile tests and hardness measurements were conducted of the ternary and comparatively of a binary non-hardenable Fe-10Mn alloy. Isothermal aging of the binary steel led to a decrease in strength along with a considerable increase in uniform elongation. The Pd-containing alloy, on the other hand, showed significant age-hardening and an embrittlement and de-embrittlement transition was revealed. Ductile behavior was observed in the initial as-quenched and over-aged state, but zero tensile elongation in the intermediate under- and peak-aged region, where intergranular fracture along the PAGBs occurred. In the brittle peak-aged state a large number of small nm-sized particles rich in Mn and Pd formed inside the grains and decorated the PAGBs. The precipitates grew in size on prolonged aging. Mn segregation to the PAGBs was revealed, and the Mn-concentration level at the boundaries varied with aging time and was highest in the peak-aged condition. Embrittlement and de-embrittlement mechanisms are discussed and compared to these observations.

**5.1 Introduction**

Maraging steels are a special class of ultra-high strength steels which harden via the formation of small nm-sized intermetallic precipitates. A variety of maraging alloys have been developed in the past. The classical representatives of this steel family are the so-called 18 wt.% Ni maraging steels, which exhibit an outstanding combination of high strength and high fracture toughness but also good machining properties [1, 2]. According to a design strategy following metallurgical, electrochemical, and toxicological considerations [3], we developed the martensitic alloy Fe-10Mn-1Pd (in wt.%) as a prospective biodegradable implant material. The alloy is intended to exhibit an enhanced corrosion rate in physiological environment to overcome the main drawback of Fe alloys in the field of biodegradable metals, i.e. their low degradation rate [3]. High mechanical
strength are also desirable, because smaller implant dimensions would then be feasible and therefore less material would need to degrade.

Fe–Mn alloys feature transformation characteristics similar to those of Fe–Ni alloys, resulting in the formation of lath martensite under most cooling conditions [4, 5]. Ternary Fe–Ni–Mn alloys show considerable age-hardening, comparable with 18 wt.% Ni maraging steels [6]. It was also observed for Fe-10Mn-1Pd [7] that, similar to Fe–Ni–Mn [6] and Fe–Pt–Mn [8] alloys, nm-sized precipitates rich in Mn and Pd form during isothermal aging at temperatures between 300-500 °C. These precipitates considerably strengthen the material. In addition, cytotoxic investigations of Fe–Mn [9], Fe–Pd [10] and Fe–Mn–C–(Pd) [11] alloys confirmed an appropriate biocompatibility. Thus, the combination of enhanced degradation rate and high strength together with suitable biocompatibility makes the Fe-10Mn-1Pd maraging steel attractive for biodegradable implant applications.

However, Fe–Mn [12-15] and Fe–Ni–Mn [16-23] embrittle after aging in the temperature range of 300-500° C. This is accompanied by premature failure in tensile tests and low-energy fracture along prior austenite grain boundaries (PAGBs). The embrittlement in binary Fe–Mn steels was associated with Mn segregation to PAGBs [14, 15, 24, 25] and it was shown that manganese is at least as effective as phosphorous in inducing embrittlement [26]. In the case of ternary Fe–Ni–Mn maraging steels, severe embrittlement appears even after short aging treatment, i.e. in the under- and peak-aged region. Controversies exist in literature as to the source of the grain-boundary embrittlement of these hardenable alloys.

In addition to Mn segregation [16, 17, 19, 20], embrittlement mechanisms related to the evolving particles were proposed such as: (i) interaction of dislocations with coherent particles inducing planar slip or inhomogeneous plastic flow [18, 23]; and (ii) the formation of coarse precipitates at PAGBs [21, 22].

In the past, most investigations on Mn segregation to PAGBs were performed using Auger electron spectroscopy (AES) [14, 15, 17-20, 24-27]. Atom probe tomography (APT) is an alternative powerful technique which is capable to spatially resolve the local chemical composition on the atomic scale. It has been widely used to investigate metals and in particular systems which show fine-scale precipitation [28, 29], and also to analyze grain boundaries in steels [30, 31]. Via APT it is also possible to distinguish between 3-dimensional features such as precipitates formed at interfaces, elemental partitioning on either side of embedded grain boundaries, or triple points within structures. Focused ion beam (FIB) based
sample preparation methods have been successfully applied to fabricate site-specific atom probe specimens of regions such as grain boundaries [32-34].

In the present study the mechanical performance of a binary Fe–Mn (Fe-10Mn) alloy and the ternary Fe–Mn–Pd (Fe-10Mn-1Pd) alloy were evaluated as a function of isothermal aging time at 500 °C. The microstructural changes, in particular at PAGBs, of the hardenable Pd-containing steel were characterized in the peak-aged and over-aged conditions via APT. Herewith we were able to correlate the microstructure and mechanical properties of these alloys.

5.2 Experimental procedure

Casts of 1 kg of the two alloys with the nominal composition Fe-10Mn and Fe-10Mn-1Pd (in wt.%) were prepared from pure elements (Fe: Armco; Mn: 99.9%, Alfa Aesar, Germany; Pd: 99.95%, UBS, Switzerland) by vacuum induction melting under 300 mbar argon atmosphere (99.998 purity). The cylindrical ingots of 35 mm diameter were then forged down to a diameter of 12 mm at approximately 1000 °C. Afterwards, the rods were cold-swaged to a diameter of 6 mm, with an annealing treatment at 900 °C for 10 min after each swaging step, to remove stresses. Finally, the rods were encapsulated in quartz tubes under 215 mbar argon atmosphere and solution-heat-treated (SHT) at 1150 °C for 12 h, followed by water-quenching. The resulting prior austenite grain size was about 100 μm. Isothermal aging of the as-quenched alloys was subsequently performed at 500 °C in air for various periods (up to 30 h). This aging temperature was deliberately chosen to achieve similar hardness values in the under-aged and over-aged states in reasonable time periods [7].

In order to evaluate the aging response of the heat-treated materials, Vickers hardness (HV10, indentation time 6s) was measured using a Brickers 220 hardness tester (Gnehm, Switzerland). The mechanical performance of the two alloys was further evaluated via standard [35] tensile testing (Schenck-Trebel, Germany) using cylindrical specimens of 2 mm diameter with a gauge length of 12 mm at a strain rate of $10^{-3}$ s$^{-1}$. Specimens in the initial as-quenched state (SHT) and after isothermal aging at 500 °C for 5 min (5min/500°C), 30 min (30min/500°C) and 30 h (30h/500°C) were tested. Fracture surfaces of broken tensile specimens were investigated via scanning electron microscopy (SEM, Hitachi SU-70). For phase identification, X-ray diffraction (XRD) measurements (PANalytical, X’Pert Pro) were conducted using Cu $K_{\alpha}$ ($\lambda = 0.15406$ nm) radiation operating at 45 kV and 40 mA with a step size of 0.01° and a time per step of 1 s. A diffracted beam monochromator was used to reduce fluorescence effects.
Fig. 5.1. Site-specific APT sample preparation of a PAGB. (a) EBSD overview map: PAGB and packets of lath martensite are visible (step size 2 μm, indexing rate 90%). (b) Higher resolved EBSD map of the area indicated by the white dashed rectangle in (a). The black dashed rectangle indicates the region of interest cut out by FIB (step size 0.1 μm, indexing rate 92%). (c) FIB-milled wedge containing the PAGB. (d) Top view, alignment of the sample wedge on a post of a micro-tip array. (e) Pt is used to weld the wedge on the post. A cross-section cut from the sample wedge mounted on the micro-tip post reveals the PAGB. (f) Final APT tip sharpened by successive annular milling.

The local chemical composition of the PAGBs was characterized by APT. Samples of the alloy Fe-10Mn-1Pd isothermally aged for 30 min (peak-aged) and 30 h (over-aged) at 500 °C were investigated. Samples were cut from the heat-treated rods, ground and finally polished using a colloidal aluminum oxide suspension (Buehler, MasterPrep). FIB-based APT specimen preparation of the PAGBs was performed using the well-established lift out method [32, 33]. Figure 5.1 shows the successive steps involved in FIB-based APT sample preparation. In order to localize the particular PAGBs of interest, electron backscatter diffraction (EBSD) scans were performed on the polished samples using a Hitachi (SU-70) SEM equipped with a Nordlys EBSD camera operated at 20 kV (Fig. 5.1a,b). A dual beam FIB (FEI, Helios 600i) was used to cut out a triangular wedge which includes the particular grain boundaries of interest (Fig. 5.1c). The sample wedge was transferred to multiple posts. Final sharpening of the tips was performed by annular milling (Fig. 5.1f). At least three APT specimens of the same PAGB of each material state were prepared in this way. The datasets with the most useful statistics (highest number of collected atoms) were used for the analysis. The APT experiments were
performed on a LEAP™ 4000X HR ( Cameca ) instrument in laser mode (wavelength 355 nm), using a specimen temperature of ~ 24 K, with a pulse frequency of 250 kHz and a constant detection rate of 1%. Data processing was conducted using the IVAS 3.6.4 software package ( Cameca ) [36-38].

5.3 Results

5.3.1 Mechanical tests

![Graph of hardness vs. time](image)

Fig. 5.2. Hardness as a function of aging time at 500 °C. For Fe-10Mn-1Pd the typical age-hardening behavior of maraging steels is observable. The black arrows indicate the time points used for the tensile tests.

Figure 5.2 displays the hardness evolution as a function of aging time at 500 °C for both alloys investigated. For Fe-10Mn the hardness gradually decreases with progressing aging time. In contrast, Fe-10Mn-1Pd shows the typical behavior of a maraging steel: rapid increase in hardness until the peak value is reached, followed by a slow decrease in hardness on prolonged aging [1].

Tensile tests on the hardenable steel were conducted in the SHT state, and in the under-aged (5min/500 °C), peak-aged (30min/500°C) and over-aged (30h/500°C) conditions. The same heat-treated states were also investigated for the Pd-free counterpart. Figure 5.3 presents the stress-strain curves of both alloys investigated, and Table 5.1 summarizes the related mechanical properties. On progressive aging of Fe-10Mn the ultimate tensile strength (UTS) decreases, in accordance with the hardness measurements, and the uniform elongation (ε_u) and the elongation at fracture (ε_f) increase (Fig 5.3a). For the binary alloy it is
Fig. 5.3. Engineering stress-strain curves of (a) Fe-10Mn and (b) Fe-10Mn-1Pd in the SHT state and after aging at 500 °C for 5 min, 30 min, and 30 h. The insert in (a) shows a comparison of the tensile curves of both investigated alloys aged for 30 h at 500 °C. The inserts in (b) reveal SEM images of fracture surfaces of Fe-10Mn-1Pd in the (1) under- and (2) over-aged states. Intergranular fracture, which occurs along PAGBs, is visible in the under-aged condition, and a ductile dimple fracture is apparent in the over-aged case.

Table 5.1. Results of the tensile tests (at room temperature) presented in Fig. 5.3 for the investigated alloys in the SHT state and after aging at 500 °C for 5 min, 30 min and 30 h.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>$\varepsilon_u$ (%)</th>
<th>$\varepsilon_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10Mn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHT</td>
<td>627 ± 45</td>
<td>961 ± 40</td>
<td>4.5 ± 0.7</td>
<td>11.9 ± 1.1</td>
</tr>
<tr>
<td>5min/500°C</td>
<td>797</td>
<td>908</td>
<td>7.2</td>
<td>18.5</td>
</tr>
<tr>
<td>30min/500°C</td>
<td>771 ± 4</td>
<td>898 ± 10</td>
<td>8.6 ± 0.4</td>
<td>17.3 ± 0.8</td>
</tr>
<tr>
<td>30h/500°C</td>
<td>609 ± 11</td>
<td>785 ± 12</td>
<td>9.7 ± 0.5</td>
<td>19.2 ± 1.0</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHT</td>
<td>662 ± 13</td>
<td>1060 ± 14</td>
<td>5.5 ± 0.8</td>
<td>12.4 ± 1.2</td>
</tr>
<tr>
<td>5min/500°C</td>
<td>---</td>
<td>---</td>
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</tr>
<tr>
<td>30min/500°C</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>30h/500°C</td>
<td>1076 ± 6</td>
<td>1198 ± 42</td>
<td>5.5 ± 0.4</td>
<td>11.7 ± 1.7</td>
</tr>
</tbody>
</table>

Interesting to note that after only 30 min of aging at 500 °C, $\varepsilon_u$ has nearly doubled compared to that of the SHT state. For Fe-10Mn-1Pd in the SHT condition it was possible to measure complete tensile test curves, revealing a behavior comparable to that of the Pd-free counterpart. In contrast, the samples of the Pd-containing alloy subjected to aging for 5 min (under-aged) and 30 min (peak-aged) at 500 °C showed serious embrittlement and premature failure in the elastic regime. However, after aging the Fe-10Mn-1Pd alloy for 30 h at 500 °C (over-aged) the ductility recovers and $\varepsilon_u$ is similar to that of the SHT state.
(Fig. 5.3b). The insert in Fig. 5.3b shows SEM images of fracture surfaces of Fe-10Mn-1Pd. Intergranular fracture occurring along PAGBs is visible in the under-aged state (1), and a typical ductile dimple fracture is apparent in the over-aged case (2). It may be noted here that although the specimens of Fe-10Mn-1Pd aged for 5 min and 30 h exhibit comparable hardness (see Fig. 5.2), they demonstrate completely different plastic behavior in the tensile tests. The insert to Fig. 5.3a compares the stress-strain curves of the binary and ternary alloys aged for 30 h at 500 °C. A remarkably different behavior of the two steels is apparent. In this heat-treatment condition the hardenable steel reveals a UTS of around 1.2 GPa and still exhibits good ductility with a total elongation of ~12 %.

5.3.2 X-ray diffraction

![XRD patterns](image)

**Fig. 5.4.** XRD patterns for Fe-10Mn-1Pd in the SHT state and after aging for 30 min (peak-aged) and 30 h (over-aged) at 500 °C. Additional peaks resulting from austenite are visible for the specimen aged for 30 h at 500 °C.

The XRD spectra of both alloys investigated showed identical characteristics and thus only the patterns for the hardenable alloy are depicted. In the initial SHT condition and after aging for 5 min (not shown) and 30 min at 500 °C only the presence of the body-centered cubic (bcc) α-phase was revealed (Fig. 5.4). Additional weak peaks resulting from austenite were observed for the specimens in the over-aged state (30h/500°C, Fig. 5.4).
5.3.3 Atom probe tomography

Site-specific APT measurements of PAGBs were performed for Fe-10Mn-1Pd in the peak-aged (30min/500°C) and over-aged (30h/500°C) conditions. Because of the high amounts of alloying elements, pole structures revealing particular lattice planes were not identifiable and thus could not be referenced for a lattice-based reconstruction. In this work, correlations between EBSD and FIB imaging were thus used to confirm the site-specific analysis. EBSD defined the specific GBs of interest, while both electron and ion beam images confirmed the GB residing within the top ~100 nm of the specimen apex for analysis.

5.3.3.1 Fe-10Mn-1Pd peak-aged condition (30min/500°C)

Figure 5.5 presents the APT results obtained for Fe-10Mn-1Pd in the brittle peak-aged state (30min/500°C). Figure 5.5a shows a longitudinal cross-section only of the reconstructed Mn-atom positions. A planar region enriched in Mn is observed which runs from top to bottom (upper half highlighted by two dotted lines). On the adjacent left side of that zone a narrow region depleted in Mn is recognizable (upper half highlighted by a dashed line; Fig. 5.5a). Fig. 5.5b presents the lower part of the reconstructed data, as indicated by the insert, in a top view. The atom positions of Mn (red) and Pd (blue) are shown. A band including a Mn-enriched and depleted region (highlighted by two dotted and a dashed line, respectively) is visible. It is assumed that the Mn segregation indicates the location of the PAGB, because Mn segregation to PAGBs during aging at temperatures between 375-500 °C is known to occur in Mn-containing steels [14, 18, 19, 26].

The isoconcentration surface method [39, 40] is a technique often used in the analysis of APT data to delineate regions of interests such as precipitates or interfaces. Because the evolved particles are enriched in Pd [7], Pd isoconcentration surfaces (blue) are used in Fig. 5.5c to highlight the precipitates. A Mn isoconcentration surface (red) is also displayed, highlighting the PAGB. A large number of precipitates has formed within the grains but precipitates can also be seen at the Mn-enriched zone, decorating the PAGB. Within the Mn-depleted zone, however, no precipitates are observable and obviously a narrow precipitation-free zone has formed. Based on the Pd isoconcentration value of 2.5 at.%, a volume equivalent radius of a sphere ($r_{\text{equ},30\text{min}}$) of 1.9±0.7 nm and a number density ($n_{d,30\text{min}}$) of $5.4 \times 10^{23}$ m$^{-3}$ of the precipitates were measured. This Pd isoconcentration
Fig. 5.5. APT results for Fe-10Mn-1Pd in the peak-aged condition. Atom maps (a-e) and proxigrams (f.g) are displayed. (a) Longitudinal cross-section of the reconstructed data. Only Mn atoms (red) are depicted. A narrow strip enriched in Mn is observable which runs from top to bottom (highlighted by two dotted lines). On the left side, adjacent to the enriched strip, a Mn-depleted zone can be observed (highlighted by a dashed line). The insert indicates the data taken for the cross-section depicted. (b) Top view of the part indicated by the insert. Mn (red) and Pd (blue) atoms are depicted. A narrow zone enriched and depleted in Mn is visible running through the entire vertical length of the depicted data. Pd is enriched in distinct zones indicating the precipitates. (c) In addition to Mn atoms (red), Pd isoconcentration surfaces of 2.5 at.% (blue) highlighting the formed precipitates and a Mn isoconcentration surface of 12.3 at.% (red), of the Mn-enriched interface only, are depicted. (d) C and (e) N atom map of the same data as depicted in (b). Segregation of these elements to the PAGB is observable. (f) Results of the proxigram analysis for Fe, Mn and Pd. The insert shows a Mn atom map of the same view of the data as depicted in (b). The Mn isoconcentration surface of 8 at.% used for the proxigram analysis is displayed. The white arrow indicates the analysis direction of the proxigram. (g) Results for Mn, C, N and P. The gray lines indicate the data points used to evaluate the composition at the various sites.

Threshold was selected because it is 5 times higher than the nominal composition. In this case the Pd-enriched zones and the number density of the precipitates remained stable when varying the value at around 2.5 at.%. Note that the dimensions of the particles are sensitive to the choice of the isoconcentration value defined by the person performing the
analysis. Thus the calculated value is an estimate, but can still serve as a clear indicator of microstructural changes.

Figs. 5.5d and e show that segregation of the impurities C (Fig. 5.5d) and N (Fig. 5.5e) within the Mn-enriched zone is also observed, but no distinct enrichment of the impurity P was recognizable. These elements are known to have either a beneficial (C, N) or detrimental effect (P, N) on the grain-boundary strength [25, 26, 41, 42].

To assess the segregation at the PAGB the proxigram analysis method [43] was used, which due to its statistically superior approach regarding 3-D features is capable of revealing the enrichment of minor solute elements and also gives high confidence in the concentration values for major alloying elements. To reveal the Mn content of the PAGB only, before the proxigram analysis the precipitates were cut out of the reconstructed volume using Pd isoconcentration surfaces. Fig. 5.5f reveals an asymmetrical Mn-concentration profile across the PAGB. The Mn-depletion on the left side of the PAGB within the precipitation-free zone decreases to a value of 5.2±0.2 at.% and the Mn-enrichment of the interface increases up to 14.3±0.2 at.% (Fig. 5.5g). The Mn-segregated zone exhibits a width of ~3 nm (considering the full width of half maximum measured above the base concentration; Fig. 5.5g). This value accords with other APT investigations on grain boundaries of metallic systems [30]. It should be noted here that the dimension of the PAGB can be overestimated due to local magnification effects [44]. The concentration of the impurities C and N at the PAGB was around 6 and 3 times higher, respectively, compared to the matrix content (Fig. 5.5g). However, their absolute concentrations at the PAGBs are low. No segregation of the impurity P was revealed in the proxigram.

5.3.3.2 Fe-10Mn-1Pd over-aged condition (30h/500°C)

Figure 5.6 presents the results for Fe-10Mn-1Pd in the ductile over-aged state (30h/500°C). A narrow strip enriched in Mn is observable, indicating the position of the PAGB (Fig. 5.6a,b). The upper half of that zone is highlighted by two dotted lines. Pd isoconcentration surfaces of 2.5 % (Fig. 5.6c) were again used to highlight the precipitates. According to Ref. [7], in the over-aged state the precipitates have increased in size ($r_{equ,30h} = 3.5±1.0$ nm) and their number density ($n_{d,30h} = 1.1 \times 10^{23}$ m$^{-3}$) has decreased compared to that in the peak-aged condition. A precipitation-free zone, occurring on one side of the PAGB, is recognizable
Fig. 5.6. APT results for Fe-10Mn-1Pd in the over-aged condition. Atom maps (a-e) and proxigrams (f,g) are displayed. (a) Slightly tilted top view of the reconstructed data. Only Mn atoms (red) are depicted. A narrow strip enriched in Mn is observable (highlighted by two dotted lines). (b) Tilted side view of the reconstructed Mn atom positions. The narrow strip enriched in Mn is recognizable, exhibiting an inclination (indicated by two black arrows). (c) In addition to Mn atoms (red) Pd-isoconcentration surfaces of 2.5 at.% (blue) highlighting the formed precipitates and a Mn-isoconcentration surface of 7.2 at.% (red), of the Mn enriched zone only, are depicted. (d) C and (e) N atom maps of the same data as depicted in (a). Slight enrichment of these elements at the PAGB is visible. (f) Results of the proxigram analysis for Fe, Mn and Pd. The insert shows a Mn atom map of the same view of the data as depicted in (a), and a Mn isoconcentration surface of 4 at.% used for the proxigram analysis is displayed. The white arrow indicates the analysis direction of the proxigram. (g) Results for Mn, C, N and P are shown. The gray lines indicate the data points used to evaluate the composition at the various sites.

(Fig 5.6c). Minor enrichments of C (Fig 5.6d) and N (Fig. 5.6e) at the PAGB were noticeable by visual inspection but no distinct enrichment of P was observed.

Fig. 5.6f,g presents the proxigram of the PAGB. Prior to analysis the precipitates were again cut out of the data set. The Mn-matrix content in both grains decreased considerably, to a value of ~5 at.%. Compared to the peak-aged condition the Mn-profile across the PAGB is more symmetrical, but on the left side of the PAGB (also the location of the precipitation-free zone) a region more depleted in Mn can still be observed. The enrichment of Mn at the PAGB was measured at up to 8.2±0.2 at.% (Fig. 5.6g).
5.4 Discussion

The main focus of this work was to relate the microstructural changes of the hardenable alloy Fe-10Mn-1Pd upon aging to its mechanical properties. In the following we first discuss the results for the binary alloy and then those for the hardenable alloy.

5.4.1 Fe-10Mn

Binary Fe–Mn alloys are susceptible to a kind of temper embrittlement which occurs if the steels are tempered or slowly cooled through the temperature range of 300 to 500 °C [12-15]. The embrittlement is characterized by intergranular fracture occurring along PAGBs and a considerable increase in the ductile-to-brittle transition temperature (DBTT) upon aging. Normally, temper embrittlement in low-alloyed steels is associated with segregation of impurities, such as Sb, Sn and P, which weaken the boundaries [45, 46]. With respect to Fe–Mn alloys, however, the segregation of Mn itself to the grain boundaries could be the reason. For a low-alloyed Fe–Mn steel containing 1 wt.% Mn, Yu-Quing et al. [26] showed that the embrittlement effect of Mn is of similar importance to that of P. For Fe-8Mn [14], which exhibits a microstructure similar to the alloys investigated here, and also for Fe-12Mn [15], it was demonstrated that embrittlement is caused by segregation of Mn to the PAGBs.

Also from a theoretical point of view, Mn on its own was shown to be an embrittling element in iron [42, 47, 48].

During the tensile tests on Fe-10Mn in the initial SHT state and after aging for 5 min and 30 min at 500 °C (Fig. 5.3a), a decrease in UTS along with a considerable increase in ductility was obtained. A similar result was observed by Ponge et al. [49], when investigating a binary Fe-9Mn alloy aged at 450 °C. With respect to the above literature concerning embrittlement of binary Fe–Mn steels, these findings may contrast at first glance. However, the apparent DBTT depends on strain rate (high rate - notch bar impact tests; low rate - tensile tests) and also on the applied stress states (multiaxial - notch bar impact tests; uniaxial - tensile tests) during testing. Both high loading rates and multiaxial stress states cause the DBTT to shift to higher temperatures. Hence it can be concluded that the DBTT for the tensile tests of the Fe-10Mn specimens was below RT, although weakening of the PAGBs due to Mn segregation presumably occurred.

Even within the first 30 min of aging of Fe-10Mn at 500 °C, $\varepsilon_u$ increased in our case considerably (Fig. 5.3a and Table 5.1) compared to the SHT state. During this tempering...
period no additional peaks resulting from newly formed phases (є or ε-martensite) were revealed in the XRD patterns. Ponge et al. [49] also noticed a significant increase in the ε₀ of their Fe-9Mn alloy upon aging at 450 °C. A reduction of micro-strains to 50% of their initial value was observed after tempering for 6 h at 450 °C [49]. They concluded that micro-creep and a possible recovery of the dislocation structure were responsible for the beneficial effect on ductility. It is thus suggested that the increase in ductility observed here after short aging (5, 30 min) is also a result of recovery processes.

After 30 h of aging at 500 °C, minor amounts of austenite were detected. In our study. Austenite is known to transform to ε-martensite and/or α'-martensite after deformation [14, 49, 50]. However, no clear transformation-induced plasticity (TRIP) effect was observed in the tensile test. In addition, the ε₀ for the specimen aged for 30 h at 500 °C increased only slightly compared to the material aged for 30 min. In this context, Tomota et al. [51], who investigated tensile properties of binary Fe–Mn alloys containing 16 to 36 wt.% Mn, stated that TRIP effects are not expected to be important for binary Fe–Mn alloys, because it is difficult to obtain a suitable transformation rate. However, the situation is different in Fe-Mn-based steels containing further alloying elements such as C, Al or Si, where the austenite has a higher stability upon mechanical deformation [52, 53].

5.4.2 Fe-10Mn-1Pd

In contrast to Fe-10Mn, the Pd-containing alloy showed significantly different mechanical performance. As described in Ref. [7] the hardness evolution of Fe-10Mn-1Pd, which is similar to that obtained for maraging steels, was associated with the formation of nm-sized precipitates enriched in Mn and Pd. A ductile-brittle-ductile transition upon aging was observed in the tensile tests for Fe-10Mn-1Pd. A similar behavior has been observed in other maraging alloys, in particular in the Fe–Mn–Ni system. In the literature basically two explanations for this embrittlement have been proposed: (i) segregation of Mn to the PAGBs; and (ii) a mechanism related to the formation of precipitates. In the following these two aspects are discussed separately.

5.4.2.1 Mn segregation as source of embrittlement

Squires et al. [16] first suggested Mn segregation as the source of embrittlement for the alloy Fe-12Ni-6Mn. Later, Feng et al. [17] confirmed via AES measurements, also on Fe-12Ni-6Mn, that Mn segregated to the PAGBs. Heo et al. reported for an Fe-8Mn-7Ni [19] and an
Fe-6Mn-12Ni [20] alloy a ductile-brittle-ductile transition upon aging. They observed that the Mn concentration at the PAGBs varied upon aging, passing a maximum in the brittle region. In comparison, the fracture strength measured in tensile tests showed an inverse trend. Consequently, embrittlement and de-embrittlement were ascribed to Mn segregation to the PAGBs and its de-segregation into the matrix. Heo [54] also theoretically analyzed the nonequilibrium segregation behavior of Mn. He showed that the time-dependent concentration variation at the PAGBs can be related to the evolving precipitates, enriched in Mn and Ni, which act as a sink for Mn.

APT results obtained for Fe-10Mn-1Pd in the peak-aged condition (Fig. 5.5) show Mn-enrichment at the PAGB up to ~14 at.%. This value agrees with those observed by Nikbakht et al. [14] for a binary Fe-8Mn steel (~18 at.% Mn, after only 6 min at 450 °C), and by Suto et al. [18] for a Fe-12Ni-6Mn alloy (~16 at.% Mn, after 20 min at 375 °C). However, the value obtained via AES by Heo et al. [19] for the Fe-8Mn-7Ni alloy was considerably higher (~32 at.% Mn, after 30 min at 450 °C). In TEM investigations in Ref. [21], coarse second phase particles rich in Mn and Ni were observed at PAGBs after 30 min of aging at 450°C for the same alloy (Fe-8Mn-7Ni). In AES measurements it is not possible to distinguish between such coarse precipitates and the segregation of Mn to the PAGBs itself. This may result in an overestimation of the degree of Mn segregation.

In the over-aged state (Fig. 5.6) the Mn content in the matrix and the amount of Mn segregation at the PAGB (~8 at.%) decreased compared to the peak-aged condition (~14 at.% at the PAGB). As mentioned above, Heo et al. [19, 54] also observed a time-dependent trend for the Mn segregation level at the PAGBs upon aging and related this behavior to the formation of second-phase particles rich in Ni and Mn. Ref. [7] revealed that the Mn-to-Pd ratio within the particle in the over-aged state (30h/500°C) was approximately 1:1. Assuming that every Pd atom binds one Mn atom, the overall Mn content can only be reduced by 0.53 at.% (nominal Pd content). Hence it seems unlikely that the precipitates alone can be made responsible for such depletion in Mn at the PAGBs for Fe-10Mn-1Pd.

Formation of austenite was observed in the XRD pattern (Fig. 5.4) of the alloy aged for 30 h at 500 °C. In literature contradictory statements are seen regarding the beneficial or detrimental role of reverted austenite on toughness in maraging steels [55]. In addition, in none of the studies on Fe–Mn or Fe–Mn–Ni alloys reviewed in the current work was austenite (retained or reverted) reported to prevent embrittlement or was it associated with
the recovery of ductility. However, from the Fe–Mn equilibrium phase diagram it can be seen that the evolving austenite at 500 °C must be enriched in Mn (equilibrium Mn composition of austenite at 500 °C = 20.8 wt.%) and the martensite must be depleted in Mn (equilibrium Mn composition of ferrite/martensite at 500 °C = 3.9 wt.%) compared to the initial nominal composition. In accordance with Heo et al. [15], it is suggested that the decrease in Mn content of the matrix and also the related decrease in Mn segregation at the PAGB, and hence its change with aging time, can be ascribed to the formation of austenite, which acts as a main sink for Mn. In that sense we suppose that reverted austenite indirectly influences ductility.

Another interesting observation made from the APT measurements is that in the peak-aged case, in particular, but also in the over-aged condition, the Mn concentration profiles along the PAGB have an asymmetric character (Figs. 5.5 and 5.6). In addition, the precipitation-free zone occurring on one side of the PAGB was observed to coincide with the more Mn-depleted zone at the PAGB. The formation of a precipitation-free zone occurring on one side of the PAGB was also observed by Nedjad et al. [56] in a detailed TEM analysis of a Fe-10Ni-7Mn steel, and they correlated this behavior with the formation process of the precipitates at the PAGBs. Anisotropic segregation phenomena of grain boundaries are also known to occur in polycrystalline Fe-based alloys [57]. Inhomogeneous grain-boundary segregation of nonspecific grain boundaries was reported, for example, for P [58], Mn [59], Ni [60], and Mo [58] in polycrystalline α-Fe. Suzuki et al. [61] investigated P-segregation of well-characterized grain boundaries in polycrystalline α-Fe. The amount of P-segregation was found to be large on high-index boundary planes and small on low-index boundary planes, independent of the orientation of the respective other grain boundary plane. It should be mentioned here that it was beyond the scope of this study to correlate the observed anisotropic Mn segregation with the orientation of the grain boundary planes. However, anisotropic segregation seems to be a plausible explanation.

Minor enrichment of C and N, but no distinct segregation of P, were observed at the PAGBs investigated (Figs. 5.5 and 5.6). However, because the concentrations of these elements at the PAGBs were very low their influence on the observed embrittlement and dembrittlement is considered to be insignificant.
To further elaborate the relationship between the evolving microstructure upon aging and mechanical properties, Yoffee diagrams were used (Fig. 5.7). These diagrams are often applied to illustrate the origin of the ductile-brittle transition in steels [62]. In Fig. 5.7a, $\sigma_F$ represents the brittle fracture strength of the material, which is usually assumed to be independent of temperature [63] and in the present case can be considered as the strength of the PAGBs. The stress states occurring in the process of a crack tip in an elastic-plastic material scales with the yield strength of the alloy, which is known to be dependent on temperature (Fig. 5.7a) and the effective yield strength ($\sigma_{YS^*}$). Because the hardness of an alloy correlates with the yield strength, $\sigma_{YS^*}$ is sometimes replaced by the hardness. From Fig. 5.7a it is apparent that below the DBTT, $\sigma_F < \sigma_{YS^*}$ and brittle behavior results; and vice
versa above the DBTT, $\sigma_f > \sigma_{YS}$, generating a ductile fracture mode. The DBTT is the temperature where $\sigma_f$ and $\sigma_{YS}$ intersect. As illustrated in Fig. 5.7a the DBTT is known to depend on the concentration of segregated impurities and also on the hardness of the material [64]. For Sb, Sn and P in NiCr steels (with the same hardness) the DBTT was shown to increase almost linearly with increasing concentration of the impurity element at the grain boundary [65]. For the same NiCr steels it was also observed that for a constant grain boundary concentration of P, the DBTT decreased as hardness decreased [66]. For Fe-10Mn-1Pd, changes in hardness and also in Mn concentration at the PAGB are observed upon aging. Specimens aged for 5 min (under-aged) and 30 h (over-aged) at 500 °C show brittle and ductile fracture behavior, respectively (Fig. 5.3); however, they exhibit similar hardness (Fig. 5.2). Hence it can be assumed that the $\sigma_{YS}$ of both specimens coincide and will shift to higher values than those of the SHT state (Fig. 5.7b). Nikbakht et al. [14] observed for the binary Fe-8Mn alloy that even after 6 min at 450 °C the Mn concentration at the PAGBs reached a saturation level of $\sim$18 at.%. Suto et al. [18] reported that the Mn segregation in their Fe-12Ni-6Mn alloys reached a saturation level of $\sim$16 at.% after only 20 min at 375 °C. Therefore Mn segregation is quite a rapid process. Although in the current work the Mn concentration at the PAGB was only measured for the specimen aged for 30 min at 500 °C, it seems to be a valid assumption that the Mn segregation level after 5 min of aging exhibits a similar degree. The maximum difference in the Mn content ($\Delta$Mn) at the PAGB (maximum Mn concentration value at the PAGB subtracted by the lowest Mn concentration value adjacent to the PAGB) changed considerably upon aging. For the peak- and over-aged states a $\Delta$Mn$_{\text{peak}}$ of $\sim$9 at.% (Fig. 5.5g) and $\Delta$Mn$_{\text{over}}$ of $\sim$5 at.% (Fig. 5.6g) can be deduced, respectively, and the $\sigma_f$ of the PAGBs will be affected as indicated in the inset of Fig. 5.7b. Hence, it can be noted from the illustration that although the specimens in the under- and over-aged conditions exhibit the same hardness, the $\sigma_f$ of the under-aged sample during tensile testing is reached first, leading to a brittle failure mode. On the other hand, the $\sigma_{YS}$ for the over-aged specimen will be reached first, resulting in ductile behavior. Accordingly, using the Yoffee diagram, it is possible to associate the embrittlement and de-embrittlement upon aging with the change in Mn concentration at the PAGB.
5.4.2.2 Precipitates as source of embrittlement

In many investigations of Fe–Ni–Mn maraging steels coarse second-phase particles located at the PAGBs were observed even in the under-aged condition. Therefore Mn segregation as a main source of embrittlement was challenged. Based on energy dispersive (EDS) measurements in a scanning transmission electron microscope (STEM), Mun et al. [21] observed no evidence of Mn enrichment at PAGBs for the investigated alloy Fe-8Mn-7Ni (aged at 450 °C for 30 min). However, coarse second-phase particles were found at the PAGBs and hence they were associated with severe intergranular embrittlement. In a later work [22] on a Fe-10Ni-5Mn alloy the occurring embrittlement and de-embrittlement upon aging was associated with the formation of fine \( \theta \)-NiMn precipitates at the PAGBs in the under- or peak-aged state and the transformation of the particles into the more thermodynamic stable austenite phase in the over-aged condition, respectively. Suto et al. [18] reported for an Fe-12Ni-6Mn steel that the maximum apparent Mn segregation level (\( \sim 16 \) at.\%) at the PAGBs was reached after 20 min of aging at 375 °C. However, grain boundary embrittlement occurred after 120 to 300 min of aging at 375 °C, at which coherent NiMn zones formed and the steel was still in the under-aged regime. The authors suggested that the interaction of moving dislocations with the coherent NiMn zones led to inhomogeneous plastic deformation and thus stress concentrations at the boundaries, resulting in the observed embrittlement. The results obtained by Nedjad et al. [23] support this. For their Fe-10Ni-7Mn alloy in the brittle peak-aged state, planar slip bands, indicating inhomogeneous plastic deformation, were seen in TEM investigations of specimens previously loaded by tensile deformation. In addition, coarse grain-boundary precipitates associated with a precipitation-free zone were observed. It was also suggested that in the ductile over-aged state the planar slip mode of fracture no longer operates because in that state dislocations bypass rather than shear the precipitates. Although Shiang et al. [27, 67, 68] studied their Fe-19.5Ni-5Mn alloy in detail using TEM, they did not report on the formation of coarse second-phase particles at the PAGBs; AES measurements revealed only weak Mn segregation to these boundaries. Thus they could not draw a clear picture of the source of intergranular fracture.

Precipitates at the PAGB are observed in the APT results for Fe-10Mn-1Pd in the peak-aged condition. Their size is not significantly different from that of the precipitates within the grains. Hence, as suggested by Mun et al. [21], the formation of coarse particles at the
PAGBs, inducing temper embrittlement, may not be the main reason here. However, it has been demonstrated for various metallic systems that lowering the ability to cross-slip and thus promoting a heterogeneous distribution of strain can strongly influence the DBTT [69, 70].

This has been shown for an equi-atomic iron–cobalt solid solution containing 2% V, where different degree of order can be produced [69]. A difference of 550 °C between the DBTT of the alloy in the disordered (DBTT_{dis} ~100°C) and ordered (DBTT_{ord} ~450 °C) material states was evaluated. In alloys containing small particles various factors can favor heterogeneous strain distribution, such as [71] (i) low stacking fault energy of the solid solution; (ii) sheared particles; (iii) short-range order, and (iv) few slip systems operating. Conversely, features that favor homogenous strain distributions are: (i) high stacking fault energy of the solid solution; (ii) by-passed particles; and (iii) many slip systems operating. In Ref. [70] the condition for crack formation (similar to that formulated by Cottrell [72]) was expressed by

$$\sigma k_s d^{1/2} \geq A \mu \gamma$$  \hspace{1cm} (5.1)

where $\sigma$ is the applied tensile stress, $k_s$ is a microscopic measure of grain-boundary hardening (in the expression of Cottrell this would be the Hall-Petch slope), $d$ is the grain diameter, $A$ is a constant, $\mu$ is the shear modulus, and $\gamma$ is the energy dissipated per unit area of crack surface. The $k_s$ parameter in the above equation is, however, a function of slip character rather than a function of interstitial locking of dislocation sources [70]; $k_s$ increases as the ability to cross-slip decreases. Therefore, to account for the altered stress concentration at the PAGBs due to the precipitates, in the Yoffee diagram depicted in Fig. 5.7c, $\sigma_{50*}$ is replaced by the product $\sigma k_s = \sigma^*$. Because of shearable particles $k_s$ is expected to be higher in the under-aged condition. Accordingly $\sigma^*$ for that heat-treatment state will be shifted to higher values compared to the over-aged case. As considered by Suto et al. [18] and Mun et al [21, 22], one may assume in our study that Mn segregation has a negligible effect on the $\sigma_{50}$ of the PAGBs, and hence in Fig. 5.7c, $\sigma_{50}$ is expected to stay constant upon aging. Thus, as indicated in Fig. 5.7c, a higher DBTT results in the under-aged specimen as opposed to the over-aged material. Accordingly, it is also plausible to attribute the observed embrittlement and de-embrittlement upon aging to the change of stress concentration due to the precipitates.
In summary, both the change in Mn segregation and the altered stress concentration at the PAGBs due to precipitation may be correlated with the observed embrittlement and de-embrittlement upon aging of the material. In both cases diffusion of Mn is incorporated, which also couples both processes. Hence, as depicted in Fig. 5.7d, it is supposed that upon aging both mechanisms will act simultaneously, leading to the observed embrittlement and de-embrittlement behavior of Fe-10Mn-1Pd. However, irrespective of the dominant embrittlement mechanisms which occur, another fact must to be concluded from the Yoffee diagrams. In the strengthened state the alloy will exhibit a DBTT which will always be higher than that of the initial as-quenched state. Consequently this may limit the applicability of the material in the hardened case.

5.5 Summary and conclusions

The mechanical performance upon aging at 500 °C of a binary Fe-10Mn steel and a ternary Fe-10Mn-1Pd maraging alloy was evaluated, and the microstructural changes at PAGBs after aging of the Pd-containing alloy were investigated using APT.

Aging of the binary alloy resulted in a decrease in UTS along with a considerable increase in uniform elongation compared to the initial as-quenched state. Even after only 30 min of tempering at 500 °C most of the ductility increase was observed. This was ascribed to recovery processes. The Pd-containing alloy, on the other hand, showed considerable age-hardening due to the formation of small nm-sized precipitates rich in Mn and Pd. An embrittlement and de-embrittlement transition was observed upon aging. This was reflected by a ductile behavior in the initial as-quenched and over-aged states, but zero tensile elongation occurred in the intermediate under- and peak-aged regions, showing intergranular fracture along PAGBs.

Site-specific APT investigations of the Pd-containing alloy revealed that in the peak-aged state a high number density of nm-sized precipitates formed both inside the grains and decorating the PAGBs. The precipitates grew in size and their number density decreased on prolonged aging. Mn segregation was observed at the PAGBs in both heat-treatment states investigated, with a considerably higher concentration of Mn at the PAGBs in the brittle peak-aged condition. The change in the Mn segregation level was attributed to the formation of austenite in the over-aged state acting as a Mn sink.
Embrittlement and de-embrittlement mechanisms proposed in literature were discussed and Yoffee diagrams were used to elaborate a relationship between the microstructure and mechanical performance. It is concluded that the combination of altered stress concentration due to precipitation and the change in Mn segregation level at the PAGBs generates the observed mechanical behavior of the hardenable Fe-10Mn-1Pd alloy.

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6 *In-vivo* degradation performance

In Chapter 5 it was revealed that Fe-10Mn-1Pd possesses high-strength in combination with acceptable ductility after isothermal aging in the over-aged regime. This would allow to considerably reduce implant dimension compared to pure Fe. Fe–Mn–Pd alloys exhibit an increased *in-vitro* degradation rate and an suitable biocompatibility was confirmed of steels containing Mn and/or Pd. Chapter 6 presents the results of an animal study, conducted with pure Fe and two Fe–Mn–Pd alloys (Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd), and discusses the fundamental aspects of their *in-vivo* degradation.
Biodegradable Fe-based alloys for use in osteosynthesis – outcome of an in-vivo study after 52 weeks

This study investigates the degradation performance of three iron-based materials in a growing rat skeleton over a period of one year. Pins of pure Fe and two Fe-based alloys (Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd, in wt.%) were implanted transcortically into the femur of 38 Sprague-Dawley rats and inspected after 4, 12, 24 and 52 weeks. The assessment was performed by ex-vivo micro-focus computed tomography, weight-loss determination, surface analysis of the explanted pins, and histological examination. The materials investigated showed signs of degradation; however, the degradation proceeded rather slowly and no significant differences between the materials were detected. We discuss these unexpected findings on the basis of fundamental considerations regarding iron corrosion. Dense layers of degradation products were formed on the implants' surfaces, and act as barriers against oxygen transport. For the degradation of iron, however, the presence of oxygen is an indispensable prerequisite. Its availability is generally a critical factor in bony tissue and rather limited there, i.e. in the vicinity of our implants. Because of the relatively slow degradation of both pure Fe and the Fe-based alloys, their suitability for bulk temporary implants such as those in osteosynthesis applications appears questionable.

6.1 Introduction

Biodegradable metals have been a subject of extensive research in the past years, and there is an ongoing interest in these materials not least because of their increasing number of potential applications [1-3]. Biodegradable materials are not only highly interesting for osteosynthesis and coronary devices, but also for degradable wound closing devices [4], tracheal stents [5] and the treatment of aneurisms [6]. Their potential is ascribed to the expectation that a degradable material will reduce the long-term risks and side effects, such as chronic inflammation, in-stent restenosis or inability to adapt to growing tissue, which are normally associated with permanent implants. Moreover, especially in the case of osteosynthesis, degradable implants require only one surgical intervention and circumvent

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the need for implant removal. They hence contribute to patient comfort and help to reduce medical costs.

In this context, biodegradable Fe-alloys are interesting candidates for such applications. The suitability of iron as a degradable implant material has been verified in preliminary in-vivo studies where stents fabricated from pure iron were investigated in animal models [7-10]. The most important results here were that no local or systemic toxicity, no early restenosis due to thrombotic processes, and no pronounced inflammation reactions were observed. The neointimal proliferation was found to be comparable to that of standard materials such as cobalt-chromium alloys and stainless steel 316L. However, the stents remained rather intact up to one year after their placement, implying that their in-vivo degradation rate was too low and the material’s performance approached that of permanent implants. Moreover, the mechanical properties of pure iron are limited and not well suited for implant materials. Consequently, a material, which shows faster in-vivo degradation and better mechanical properties, needs to be found.

Thus, this study concentrated on the development of biodegradable iron-alloys with increased degradation rate, appropriate mechanical performance and simultaneously good biocompatibility. Hermawan et al. [1] presented iron-manganese alloys with mechanical properties similar to those of stainless steel 316L and higher in-vitro degradation rates. However, the degradation rate of the iron-manganese alloys is still one order of magnitude lower than that of magnesium alloys (which represent a second class of engineering materials for degradable implants) and may still be too low for practical applications. To further extend freedom in alloy design and to achieve even higher degradation rates, a design strategy for iron-based alloys was already presented [11]. The iron-manganese-palladium alloys produced according to this approach feature excellent mechanical properties, especially high strength (Table 6.1), and a degradation rate in in-vitro experiments which is higher than those of pure iron and iron-manganese alloys [11]. The high strength values of these alloys in particular enable the realization of slender and filigree implant designs that are favorable for two reasons: first, they introduce less material into the body to degrade; and second, their degradation kinetics – slower than that of magnesium alloys – becomes tolerable because of the smaller implant dimensions.
Table 6.1. Strength values of pure Fe and different Fe-based alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (Armco)</td>
<td>230 ± 5</td>
<td>300 ± 5</td>
<td>Schinhammer et al. [12]</td>
</tr>
<tr>
<td>316L</td>
<td>290 ± 15</td>
<td>630 ± 5</td>
<td>Schinhammer et al. [12]</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>361 ± 33</td>
<td>723 ±19</td>
<td>Hermawan et al. [13]</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>234 ± 7</td>
<td>428 ± 7</td>
<td>Hermawan et al. [13]</td>
</tr>
<tr>
<td>Fe-10Mn-1Pd</td>
<td>1076 ± 6</td>
<td>1198 ± 42</td>
<td>Moszner et al. [14]</td>
</tr>
<tr>
<td>Fe-21Mn-0.7C-1Pd</td>
<td>1095 ± 35</td>
<td>1320 ± 15</td>
<td>Schinhammer et al. [12]</td>
</tr>
</tbody>
</table>

YS – Yield strength; UTS – Ultimate tensile strength

While the in-vitro degradation rate of the iron-manganese-palladium alloys exceeds that of pure iron and iron-manganese alloys, the in-vivo degradation of these materials has not so far been investigated. Moreover, the degradation rate of pure iron implants was not determined in the course of previous studies. Consequently, the present study aims to assess the in-vivo degradation of pure iron and the newly developed iron alloys. It used a rat model, where pins were transcortically implanted into the femur and monitored over the period of one year. Degradation was studied by weighing explanted specimens and complementary by determining volume-loss based on µ-CT data. Surface analysis and histological sections were also performed on the explanted samples.

6.2 Materials and methods

6.2.1 Implants

In this study three different materials were investigated (alloying content in wt. %): pure Fe (ferromagnetic, Armco quality); Fe-10Mn-1Pd (ferromagnetic); Fe-21Mn-0.7C-1Pd (paramagnetic). Details concerning production and characterization in terms of microstructure and mechanical performance for Fe-10Mn-1Pd are given in Ref. [15] and for Fe-21Mn-0.7C-1Pd in Ref. [12]. The final heat treatment of the alloys investigated here involved aging of Fe-10Mn-1Pd for 30 h at 500 °C, and aging of Fe-21Mn-0.7C-1Pd for 10 min at 700 °C. The materials were already tested in-vitro for their biocorrosion, blood compatibility and cell viability [11, 16, 17]. The implants used for the present in-vivo studies were cylindrical pins with a diameter of 1.6 mm and a length of 8 mm. After machining, these pins were cleaned with pure ethanol in an ultrasonic bath and dried in warm air. Before operation, they were weighed, and their pin volume and surface were determined via high-resolution µCT scans over a period of 52 weeks. Preoperatively all pins were sterilized by gamma radiation.
6.2.2 Experimental design

Rats were housed in groups of four in clear plastic cages on standard bedding. Water and a standard pellet diet were given *ad libidum*. The Austrian Ministry of Science and Research authorized the animal experiments (accreditation number BMWF-66.010/0087-II/3b/2011), which were all conducted under animal ethical conditions.

Thirty-eight 5-week-old male Sprague-Dawley rats with body weights of 140–160 g were used in this study. Of these, thirty-six underwent µCT scans and two were subject to histological examinations. To check correct pin position, a µCT investigation was performed within one week after operation. At four prearranged time points (4 weeks, 12 weeks, 24 weeks, and 52 weeks after pin implantation) *ex vivo* high-resolution µCT scans were also performed. For this purpose the 36 rats intended for the µCT scans were separated randomly into three groups (*n*=12, each). Under general anesthesia each rat had two identical pins of the same alloy implanted into its distal femoral bones. Thus there were 3 rats (6 femoral bones) per alloy group (*n*=3) and time point post implantation (*n*=4) for the radiological assessment.

Two five-week-old rats were used for histological investigations. Histological slices were investigated at the 36th week and limited to pure Fe pins.

6.2.3 Surgical procedure and postoperative treatment

Under general anesthesia, the pins were implanted into the femoral mid-diaphyseal region of the rats as reported in a previous study [18]. Perioperative pain-treatment was also identical to that reported in our previous study [16]. After surgery the rats were allowed to move freely in their cages without external support and with their weight bearing unrestricted. Clinical observation was performed daily throughout the study period.

6.2.4 Euthanasia

Volatile isoflurane (Forane®, Abbot AG, Baar, Switzerland) was used for general anesthesia. Subsequently, 25 mg sodium thiopental (Thiopental® Sandoz, Sandoz GmbH, Kundl, Austria) was injected into the cardiac ventricle, causing direct cardiac arrest. Immediately after harvest of the femur, all soft tissues were carefully removed. The bone implant specimen of each alloy was embedded in dry ice and the µCT scan was performed.

6.2.5 Preparation of the bone-pin model

Immediately after euthanasia, a longitudinal skin incision was made medially at each rat’s femur. After transection of the muscles, the femur bone was carefully exposed and ex-articulated at the adjacent joints. The area beneath the implant was untouched and was covered by thin laminas of remaining
tissue in order not to change the existing pin-bone conditions. Immediately after total preparation the bone was wrapped in physiological saline-solution-dipped swab material and brought to the µCT.

6.2.6 High-resolution microfocus computed tomography and image reconstruction
To determine the pin volume and the pin surface, µCT images were assessed using a Siemens Inveon™ Research Workplace “Acquisition 1.2.2.2”. The µCT scans were conducted using a polychromatic source at 80 kV voltage, 500 µA current with an exposure time of 2000 ms. Scanning was performed with no storage trays on de-wrapped samples. To reduce fluorescence a 1.5 mm thick aluminum filter was used. Images were reconstructed using the Siemens Inveon™ Workplace 3.0 software. For reconstruction beam hardening correction and filtered back projection with a bilinear interpolation and a shepp-logan filter were applied. Pins were reconstructed as 3D models, and upper and lower thresholds for the pins were set at 3256 and 8064 Hounsfield units (HU). Pin volume and the pin surface were quantified up to the 52th week, allowing observation of the degradation process within one year.

6.2.7 Determination of weight loss after explantation
The initial weight and the weight of the explanted samples after 4 weeks and 52 weeks were determined as follows. From the retrieved pins the degradation products were mechanically and chemically removed [17]. In a first step the pins were mechanically cleaned with a brush. The specimens were then ultrasonically cleaned in ethanol and subsequently immersed for 20 min in a rust-removal solution containing 11.1 g sodium dihydrogen citrate (ABCR GmbH), 1.7 g citric acid (Merck) and 0.1 g tryptamine (ABCR GmbH) in 250 ml deionized water [17]. In a last step the samples were again mechanically cleaned using a brush, ultrasonically cleaned in ethanol, and finally dried in hot air. We also checked the reliability of the cleaning procedure by using not-implanted control samples of the same alloy compositions.

6.2.8 Surface analysis
The surface of the retrieved pins was analyzed 4 and 52 weeks after implantation. After explantation of the femur, the pins were carefully removed from the bone tissue. The samples were cleaned with isopropanol in an ultrasonic bath for 10 minutes, and then dried at room temperature. The explanted pins were first inspected by optical microscopy using a stereo microscope (Leica MZ 12.5). Then the microstructure and chemical composition of the degradation products were characterized using a scanning electron microscope (SEM, Hitachi SU-70, operating at 20 kV acceleration voltage), equipped with an X-max energy dispersive X-ray (EDX; Oxford instruments) detector. For that purpose longitudinal cross-sections of the samples were prepared as follows: the implants were embedded in Bakelite and ground until approximately the middle of the pins was reached; polishing was conducted down to 1 µm
Therefore, the final polishing step was performed using 0.05 µm Al2O3 suspension (MasterPrep, Buehler). The polished cross-sections were also coated with a thin ~8 nm thick conductive carbon film to reduce charging effects within the SEM. The elemental distribution of the implant surface was mapped by EDX scans.

6.2.9 Histological processing
Histological slices were investigated at the 36th week and were limited to pure Fe. After explantation, the samples including the implants were fixed in commercial 3.5 % formalin for 5 days at room temperature. Then the tissues underwent dehydration, embedding and polymerization in methylmethacrylate (Technovit 9100 New, Heraeus-Kulzer, Hanau, Germany) according to the manufacturer’s instructions and established protocols [19]. Prior to sectioning, the implants were electrochemically removed according to a previously described method [20]. The generated cavities formerly containing the implants were refilled with Technovit 9100 New. After final polymerization, the tissue blocks were cut into 5 µm thick sections using a RM 2155 microtome (Leica, Bensheim, Germany) and placed on poly-L-lysine-coated glass slides. Slices were pressed and dried for 2 days at 37°C, then deacrylated in xylol (2 × 10 min) and 2-methoxyethylacetate (1 × 10 min), cleared through a decreasing isopropyl alcohol series (2 × 100%; 1 × 96%; 1 × 70%, 2 min each), and finally rehydrated with distilled water. Detection of Fe3+ (Prussian Blue), Fe2+ (Turnbull’s Blue) and Fe3+/Fe2+ ions (Quincke reaction) was performed as described in Romeis Mikroskopische Technik [21] and Pearse [22], respectively. Photomicrographs were taken with a Zeiss Axioskop 40 microscope combined with a Zeiss AxioCam MrC digital camera and Zeiss AxioVision software (Zeiss, Oberkochen, Germany).

6.2.10 Statistics
The statistical analysis includes the µCT data of six pins per alloy per time point. Statistical analysis was performed using IBM® SPSS® Statistics 20 (IBM Corporation, Armonk, NY, USA). Pin volume (V, mm³) and pin surface (S, mm²) were measured for each sample in the first postoperative week, then at weeks 4, 12, 24 and 52. Data did not show a normal distribution according to the Kolmogorov-Smirnov test. Therefore, statistical significant differences between the groups at each selected time point were analyzed via the Kruskal-Wallis test. To determine significant differences within each experimental group the Wilcoxon test was applied. Values were expressed as medians with minimums and maximums. A p-value <0.05 was considered to be statistically significant.
6.3 Results

6.3.1 Clinical findings

None of the animals showed signs of severe clinical pathology. *Post operationem* there was a slight swelling in most wounds for one to two days, compatible with physiological wound healing. No animal showed a sign of pathological wound inflammation and all wounds healed within time. The general health conditions of all animals were good. All rodents showed full-weight bearing immediately *post operationem* and over the whole study period. During the postoperative period, the animals developed adequately and gained weight in a physiological growth manner.

6.3.2 Determination of the in-vivo degradation

In the µCT investigations performed during the first post-operative week the µCT images showed correct transcortical implant positioning in the distal third of the femur in each rat. Each implant ran through both corticalice (medial and lateral of the femur).

![Fig. 6.1](image)

**Fig. 6.1.** 3D reconstruction of the high-resolution µCT scans after 4 weeks (a-c) and 52 weeks (e-f) of pure Fe (a, d), Fe-10Mn-1Pd (b,e) and Fe-21Mn-0.7C-1Pd (c,f). The samples show discrete haze due to µCT artifacts.

The *in-vivo* degradation was investigated via µCT scans at weeks 4, 12, 24 and 52, and weight loss measurements of explanted pins at weeks 4 and 52. Figure 6.1 presents µCT scans of the samples investigated after implantation for 4 and 52 weeks. For both time points no apparent reduction in volume was observed by visual inspection. Slight hazes were found around all samples, which hampered the visual characterization of the extent of degradation.
Fig. 6.2. (a) Mean volume and (b) mean surface area as determined from µCT scans, and (c) weight of explanted pins measured over the study period of 52 weeks. The insets in the upper two graphs show the p-values which correspond to the measured curves.

The mean volume and mean surface area of the pins measured by means of µCT scans (at weeks 4, 12, 24 and 52) are presented in Figure 6.2 a,b. The inserts display the p-values deduced from the statistical test. It can be seen that for all samples during the study period of 52 weeks no statistically significant (i.e. p-values > 0.05) loss in volume or change in surface area was observed. Even though the mass loss measurements indicate a slight decrease in the samples’ weight, the differences are not statistically significant.

6.3.3 Surface analysis

The surfaces of the samples implanted for 4 and 52 weeks were examined via optical (Fig. 6.3) and electron microscopy (Fig. 6.4). With regard to the optical micrographs of the pins after 4 weeks of implantation (Fig. 6.3 a-c) no significant differences among the samples were found. Slightly dark degradation products were recognizable on the surface; however, no distinct
Fig. 6.3. Optical micrographs of the pins after implantation for 4 weeks (a-c) and 52 weeks (d-f) of pure Fe (a,d), Fe-10Mn-1Pd (b,e) and Fe-21Mn-0.7C (c,f).

correlation between the areas where degradation took place and implantation site was observed. Occasionally, slight grooves from the machining of the implants were still visible on all samples. Figure 6.4 a-c shows the morphology and chemical composition of the cross-sections of the alloys investigated after 4 weeks. In the bottom part of the images the metal is visible followed by the degradation products, and in the upper part of the images the embedding material can be recognized. The degradation products of the pure Fe pin implanted for 4 weeks (Fig. 6.4 a) were rich in Fe and O but also contained P and Ca, and at some locations a higher concentration of Na and K was found (Fig. 6.4). For Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd implanted for 4 weeks (Fig. 6.4 b,c), the degradation products also contained Mn. An additional accumulation of Pd close to the metal-matrix surface was also observed.

After 52 weeks of implantation optical microscopy investigations (Fig. 6.3 d-f) again showed no significant differences among the alloys. Compared to the samples implanted for 4 weeks, however, more voluminous degradation products were observed and nearly the whole pin surface was covered with degradation products. In the cross-sections of the 52-week samples (Fig. 6.4 d-f) the degradation products appeared to have quite a dense character. EDX maps revealed that the degradation products consisted of two layers. In the case of pure Fe the topmost layer was always clearly enriched in P and Ca, and also contained Fe and O (Fig. 6.4 d). Some areas of the P-rich layers also contained a higher amount of Na and K. The
Fig. 6.4. SEM images of the cross-sections of the pins after implantation for 4 weeks (a-c) and 52 weeks (d-f) of pure Fe (a,d), Fe-10Mn-1Pd (b,e) and Fe-21Mn-0.7C (c,f). The left-hand images show secondary electron contrast; the right-hand images display the corresponding elemental distribution maps.
underlying layer (directly adjacent to the metal surface) was mainly composed of Fe and O (Fig. 6.4 d). In the entire cross-section, the thickness of the two layers varied, i.e. at some sides the P-rich oxide layer was directly adjacent to the metal surface. Sometimes only a pure Fe,O layer on top of the metal surface was observed.

In the case of the Mn-containing alloys (Fig. 6.4 e,f) the degradation products showed a similar layered structure. Both layers were also enriched in Mn. In both cases, an accumulation of Pd was also visible close to the metal surface. The 52-week samples showed differences in how the metal surface was attacked, which also reflects the different microstructures of the investigated alloys. For pure Fe the degradation generally proceeded homogeneously with the formation of small dimples (indicated by the black arrow in Fig. 6.4d), and no preferential attacking sites such as ferrite grain boundaries were observed. Similar degradation behavior was apparent for Fe-21Mn-0.7C-1Pd, but at some positions twin boundaries within the austenite grains (indicated by the black arrow in Fig. 6.4 f) were found to be preferential degradation sites. For Fe-10Mn-Pd shallow pits were visible (indicated by the black arrow in Fig. 6.4 e), which may reflect the martensitic microstructure of this alloy.

Cracks in the oxide layers were also observed in the SEM images of Fig. 6.4. They appear like that of “cracked earth” and are presumably a result of dehydration, which occurred during sample preparation.

6.3.4 Iron accumulation around the implants

Figure 6.5 shows the results of the histological inspection 36 weeks after implantation. The blue areas indicate the presence of Fe-ions. Both oxidation states, Fe$^{2+}$ and Fe$^{3+}$, are accumulated in the close vicinity of the implants (Fig. 6.5a; Quincke reaction). A more specific differentiation between the accumulation of Fe$^{2+}$ and Fe$^{3+}$, respectively, was achieved by using Turnbull blue and Prussian blue staining. Turnbull blue staining showed only small amounts of Fe$^{2+}$ at the bone implant interface (Fig. 6.5b). The main part of the iron accumulation was Fe$^{3+}$, as detected by the Prussian blue staining (Fig. 6.5c).

The implants are well integrated and sheathed by a narrow capsule of connective tissue. The degradation process caused no harm to the surrounding tissue, and no signs of inflammation or local toxicity were observed.
Fig. 6.5. Detection of Fe$^{3+}$/Fe$^{2+}$ (a, using Quincke reaction), Fe$^{2+}$ (b, using Turnbull blue), and Fe$^{3+}$ (c, using Prussian blue) in consecutive sections of the pure Fe samples after 36 weeks. Fe-ions were primarily located at the implant-bone interface lining the implant holes (marked by black stars). The implants were well integrated and the degradation processes caused no obvious harm to the neighboring tissues.

6.4 Discussion

For the development of biodegradable implants, reliable data on in-vivo degradation are of paramount importance. Verifiable data on the in-vivo degradation of biodegradable Fe-alloys (i.e., pure Fe and Fe-based alloys presented here) is not yet available in literature. To provide such information, the in-vivo degradation behavior of pure Fe and two Fe-based alloys (Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd) was assessed in a living rat model over a study period of 52 weeks. In the following we discuss the results of the study, the strengths and limitations of the methods employed, and the implications for future alloy development.

6.4.1 Determination of the degradation rate

The 3D reconstructions based on the high-resolution μCT scans showed slight signs of degradation. This information, combined with insights from examination of the retrieved samples and the histological sections, confirms that all samples did show some (although limited) in-vivo degradation: the optical microscopy images reveal signs of degradation on the sample surfaces and the fact that Fe-ions were detected in the histological sections reveals that there is degradation.

It is generally difficult to precisely determine small losses in volume (done here by means of μCT scans) or mass (here by weighting retrieved samples). Degradation products might be
added unintentionally to the volume of the metal when performing the evaluation of μCT scans. Although weighing is a precise method we may not be able to completely remove the degradation products during cleaning of the retrievals. μCT evaluation has continually matured over the last decades and is now a powerful tool in the evaluation of *in-vivo* studies. However, metallic materials may leave artifacts in μCT images, and beam hardening, in particular, limits the analysis and quantification of corrosion areas with little corrosion and low-density areas.

The faint hazes seen around the implants are attributed to such artifacts, which reduce the contrast of the images and obscure details [23]. In fact, we consider artifacts to be responsible for the limited accuracy in the determination of sample volume and surface area. However, it is important to state clearly that the degradation process is rather slow in the chosen *in-vivo* model.

At first glance it may appear surprising that over the period of one year so little degradation took place, especially when taking the existing literature [7-10] into account, where the results of *in-vivo* studies on stents made from pure Fe were reported. In these reports, degradation products were already found after one month. However, it is important to emphasize that until now no attempt has been made to exactly quantify the loss in material due to degradation.

### 6.4.2 Factors that influence the degradation of Fe-based materials

Not only the comparison with existing *in-vivo* studies, but also with *in-vitro* experiments reveals distinct differences. Table 6.2 summarizes the degradation rates of pure Fe and Fe-based alloys as determined by immersion tests in physiological media. From those tests it may be concluded that Fe–Mn and especially Fe–Mn–C–Pd alloys degrade significantly faster than pure Fe. However, both the *in-vivo* measurements of the implant volumes and the determination of mass loss did not indicate any differences in their degradation rate. It is thus important to consider the electrochemical processes that take place during the *in-vivo* degradation of such materials. Important conclusions may also be drawn from the conditions present *in-vivo* in the environment where the pins were implanted.
Table 6.2. *In-vitro* degradation rate of pure Fe and different Fe-based alloys determined in physiological media via weight loss measurements.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Medium</th>
<th>Degradation rate (mm/year)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>SBF</td>
<td>0.23</td>
<td>Zhu el. [24]</td>
</tr>
<tr>
<td>Fe</td>
<td>Hank’s solution</td>
<td>0.2</td>
<td>Hermawan et al. [13]</td>
</tr>
<tr>
<td>Fe-25Mn</td>
<td>Hank’s solution</td>
<td>0.5-1.1</td>
<td>Hermawan et al. [13]</td>
</tr>
<tr>
<td>Fe-35Mn</td>
<td>Hank’s solution</td>
<td>0.4-0.7</td>
<td>Hermawan et al. [13]</td>
</tr>
<tr>
<td>Fe</td>
<td>SBF</td>
<td>0.1</td>
<td>Schinhammer et al. [17]</td>
</tr>
<tr>
<td>Fe-21Mn-0.7C</td>
<td>SBF</td>
<td>0.13</td>
<td>Schinhammer et al. [17]</td>
</tr>
<tr>
<td>Fe-21Mn-0.7C-1Pd</td>
<td>SBF</td>
<td>0.21</td>
<td>Schinhammer et al. [17]</td>
</tr>
</tbody>
</table>

As pointed out in literature, the anodic partial reaction (Fe → Fe^{2+} + 2e⁻ (6.1), oxidation of the metal) usually proceeds rapidly in media [17]. In oxygen-containing aqueous solutions in the pH-range between 4 and 10, the reduction of dissolved oxygen is the cathodic partial reaction: H₂O + 1/2 O₂ + 2e⁻ → 2OH⁻ (6.2). These conditions apply to most of the potential implantation sites in a living body (except e.g. implantation in the gastrointestinal tract). The reduction reaction (6.2) and, coupled to it, the oxidation reaction (6.1) proceed as rapidly as dissolved oxygen reaches the metal surface. The availability of oxygen in a given tissue is hence a critical factor, which influences the degradation rate of an Fe-based implant *in-vivo*. This argument helps to explain the obvious differences between previous *in-vivo* studies on pure Fe, where stents were implanted in a blood vessel, and this study. The pure Fe stents degraded significantly faster than the pins investigated here. Because the underlying corrosion reaction proceeds as fast as dissolved oxygen reaches the metal surface, it can be concluded that the circulating blood provides a continuous supply of oxygen, which in turn generates a higher degradation rate. The availability of oxygen is considerably lower in the tissue in the vicinity of the pins investigated here. This may be an important reason that the degradation is much slower. However, a more detailed study is necessary in order to further elucidate this argument.

From the results of the *in-vivo* degradation experiments presented in this study it appears that oxygen availability is even more important for degradation rate than alloy composition. In contrast to laboratory tests, it was observed here that the Fe–Mn (–C)–Pd alloys *in-vivo* did not degrade significantly faster than implants made from pure Fe.

Another important factor, which influences the degradation rate, is the formation of degradation products on the implant surface. The Fe-ions, which are usually formed in the
corrosion process, react with hydroxyl ions (OH\textsuperscript{-}-ions) to form hydrous ferrous oxide (FeO\textsubscript{n}H\textsubscript{2}O). Dissolved oxygen causes the ferrous (Fe\textsuperscript{2+}) oxides to be further oxidized to ferric (Fe\textsuperscript{3+}) oxides according to the following reaction: Fe(OH)\textsubscript{2} + 1/2H\textsubscript{2}O + 1/4O\textsubscript{2} → Fe(OH)\textsubscript{3} (6.3).

In corrosion products, because of the oxygen gradient, oxidation to the ferric form usually commences in the outer layers and subsequently progresses towards the metal surface. The formation of such Fe-oxide degradation products has been observed \textit{in-vitro} [16, 17, 25], but also \textit{in-vivo} by Peuster et al. [9, 26]. The SEM investigation of the degradation products revealed that they possess a layered structure where the first layer adjacent to the metal consists of oxidized constituents of the material, i.e. Fe, Mn, Pd, and O. On top, there is a second layer that besides Fe, Mn, and O also contains elements that originate from the living organism, i.e. P, Ca, Na, and K. As pointed out above, the oxygen reduction generates OH\textsuperscript{-}-ions, leading to a local rise in the pH-value. This may in turn promote the precipitation of compounds such as FeCO\textsubscript{3} or Fe-phosphates. It is known e.g. that Fe-corrosion proceeds slower in hard water compared to soft water because the high availability of carbonates in the hard water promotes the formation of partially protective layers on the metal surface [27]. In addition, Fe-phosphate coatings are used in industry to provide protective coatings against corrosion [28]. Besides the fact that Fe-phosphates show low solubility in water, hydrous ferric oxide (Fe(OH)\textsubscript{3}) is able to bind phosphates on its surface [29]. Eventually, because the degradation products (i.e. Fe-oxides and precipitates) form on the implant surface, they affect the oxygen transport to the metal [30]. Their composition and structure (which influence the oxygen permeability) determine the extent to which they hinder the degradation process. Because of the relatively slow degradation process it can be concluded that the degradation products, which were observed to be rather dense, substantially hinder the transport of the oxygen towards the metal surface, which would be necessary for further degradation.

It may also be assumed that the implantation site and hence the different tissues in question also influence the composition of the degradation products. It is interesting to observe that the overall structure of the degradation products is to a certain extent similar to that previously found in laboratory experiments [17].

6.4.3 Iron release to the surrounding tissue

The SEM images reveal that the thickness of the degradation products after 52 weeks is on the order of 10 to 30 μm. As expected, they contain a high amount of material constituents,
such as Fe, Mn, Pd, and C. The histological sections, on the other hand, show that the tissue surrounding the implant contains a significant amount of Fe-ions. The Fe-ions were transported almost as far as 1 mm away from the implant surface. Comparing the images obtained by the different staining techniques reveals that the majority of the Fe-ions oxidized to the Fe$^{3+}$ form. This seems reasonable because dissolved oxygen in the tissue would promote the oxidation of Fe$^{2+}$ to Fe$^{3+}$ according to eq. (6.3).

6.4.4 Implications for future material development

The results obtained in this study show that Fe and Fe-based alloys that were transcortically implanted did degrade in-vivo, even if the degradation rate was rather low. Moreover, it appeared that the differences between the degradation rates of pure Fe and the Fe-based alloys designed for a faster degradation are actually negligible in in-vivo studies. Previously performed in-vitro cytocompatibility studies indicated that too much Mn release might affect the biocompatibility of Fe–Mn–C–Pd alloys [16]. The results of this study showed no signs of local toxicity; the implants were well integrated into the bone and the detection of P and Ca on the outer layer of the degradation products might indicate bioconductivity of the implants. Also no abnormal clinical observations were made post operationem. Even though the Fe–Mn(−C)–Pd alloys did not degrade significantly faster than pure Fe, they certainly provide much better mechanical properties, which allow a greater freedom in implant design. Hence, this study’s findings show that degradation of Fe-based implants is determined mainly by in-vivo conditions (i.e. oxygen availability and the composition and structure of degradation products) present in the implantation site, rather than by the composition of the material.

6.5 Summary

In this study the in-vivo degradation performance of pure Fe and two Fe-based alloys (Fe-10Mn-1Pd and Fe-21Mn-0.7C-1Pd) was assessed in a living rat model over a study period of 52 weeks. Microfocus computed tomography scans (volume and surface) and weight loss measurements of explanted samples were performed in order to monitor degradation. The surface of retrieved pins was analyzed via optical and scanning electron microscopy, and histological slices were assessed. Formation of degradation products (Fe-oxides) on the implant surface was clearly observed, demonstrating that degradation of the materials investigated took place. No post-operative
signs of local toxicity and no clinical abnormalities were observed. However, the degradation proceeded rather slowly and no pronounced reduction in volume or mass loss was apparent. In addition, the degradation rates observed for the two Fe-based alloys were not significantly higher than those of pure Fe. The observed in-vivo degradation behavior was discussed according to electrochemical considerations. It is suggested that a low oxygen content in the vicinity of the implants, coupled with visible dense degradation products which can potentially hinder oxygen transport towards the metal surface, caused the slow pace of in-vivo degradation.

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**References**

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7 Summary and Outlook
7.1 Summary

The aim of the current thesis was to develop and comprehensively characterize a new class of Fe–Mn–Pd alloys suitable for biodegradable implant applications. The development is based on a design strategy which results in alloys meeting the requirements of biocompatibility along with an enhanced in-vitro degradation rate in physiological environment.

In addition, in order to reduce implant dimensions in particular the development of a high-strength material was aimed at. In that respect martensitic (α’-martensite) Fe-based alloys containing 5 and 10 wt.% Mn with the addition of 1 to 6 wt.% Pd showed a very pronounced hardening behavior after isothermal heat-treatments (aging) at temperatures in the range between 300 to 500 °C. This is for example impressively reflected by the alloy Fe-10Mn-6Pd which in the peak-aged state \(HV_{\text{Fe-10Mn-6Pd}}^{\text{peak-aged}} = 735\) exhibits more than 700% higher hardness compared to pure Fe (Armco quality, \(HV_{\text{Fe}} = 100\)). Assuming cylindrical implant geometry, by using the Pd-containing alloy it would be possible to reduce the implant diameter by roughly 60% compared to pure Fe, and accordingly \(\approx 85\% \) less material would need to degrade. The strengthening behavior of the Fe–Mn–Pd alloys upon aging was related to the formation of Pd and Mn-rich precipitates forming within the α’-martensite matrix. It was shown that the martensitic Fe–Mn–Pd alloys can be classified as maraging steels. The observed precipitation sequence was found to be similar to Fe–Mn–Ni and Fe–Mn–Pt maraging steels, i.e. formation of coherent zones in the under-aged region and precipitates having a chemically ordered (CuAu-type) face-centered tetragonal structure in the over-aged material state.

During aging, in addition to precipitation the α’-martensite matrix partially transforms to austenite (γ). The overall transformation characteristics of binary Fe–Mn and ternary Fe–Mn–Pd alloys was assessed upon fast and slow continuous heating. This was done in order to comparatively study the precipitation reaction and the mechanism involved in the reverse \(\alpha' \rightarrow \gamma\) transformation. The following important aspects were established: (i) Below a certain temperature \(T_0\) (temperature where the Gibbs free energy of α’ equals that of γ) austenite can only evolve through long-range diffusion of Mn; (ii) during fast heating the reversion from martensite to austenite can be considered as partitionless and the interface-controlled reaction appears in a single stage; (iii) upon slow heating the \(\alpha' \rightarrow \gamma\) transformation splits up
into two consecutives stages. During the first stage, the austenite formation is dominated by long-range diffusion of Mn. In the second stage the austenite reversion occurs via a predominantly interface-controlled mechanism; (iv) the precipitation reaction was seen to proceed and affect the reverse $\alpha' \rightarrow \gamma$ transformation. It was elaborated that the main effect of the precipitates is to impede austenite growth, in particular when austenite is formed in an interface-controlled mode.

Furthermore, the influence of isothermal aging at 500 °C on the mechanical properties of Fe-10Mn and Fe-10Mn-1Pd were determined using tensile tests. For Fe-10Mn recovery processes occurred during the isothermal heat treatment, which lead to a decrease in ultimate tensile strength (UTS) along with a considerable increase in uniform elongation. In contrast to that, Fe-10Mn-1Pd experienced severe embrittlement during aging in the under- and peak-aged regimes. However, during over-aging tensile ductility recovered, resulting in a condition characterized by simultaneously high strength (UTS $\approx$ 1200 MPa) and suitable ductility (elongation at fracture $\approx$ 12%). The embrittlement and de-embrittlement behavior of Fe-10Mn-1Pd was related to two processes simultaneously occurring during aging: (i) Formation of precipitates and their interaction with dislocations in the under-aged state (dislocation cutting of precipitates, leading to a decrease of cross-slip ability) and over-aged state (dislocation looping of precipitates, leading to a recovery of cross-slip ability); (ii) Mn-segregation to prior austenite grain boundaries (PAGBs) and its change with aging time. The Mn-concentration level at the PAGBs was observed to be highest in the peak-aged state and lower in the over-aged condition.

Finally, in an animal study the degradation behavior of Fe, Fe-10Mn-1Pd and a Fe-21Mn-0.7C-1Pd was evaluated. An unexpected low degradation rate was observed for all alloys investigated and no differences were found between the materials. Considering the fundamentals of Fe degradation, the dissolved oxygen content within the physiological environment and its transports towards the metal surface appeared to be of significant importance. It is suggested that low oxygen content in the vicinity of the implants, in combination with dense degradation products on the implant surface potentially hindering oxygen transport towards the metal surface, caused the slow rate of \textit{in-vivo} degradation. In this respect, the application of Fe-based alloys as biodegradable implant materials appears questionable.
However, it should be emphasized that the metal-physical insights gained are not restricted to the Fe–Mn–Pd system but may also contribute to a better understanding of other high strength Fe–Mn-based maraging steels.

7.2 Outlook

Maraging steels are widely used in industry and Fe–Mn-based systems are considered as very interesting materials in steel research. Computer-aided alloy development also belongs to the future trends in modern steel research. In the current work the overall transformation process upon continuous heating of binary Fe–Mn alloys was successfully reproduced by using the simulation solid-state software MatCalc. In this context, it would be very interesting to compare predictions from simulation regarding processing (heat-treatment within the ferrite-austenite phase field) and evolving microstructure (mean austenite, martensite grain size and their chemical composition) with experimental observations. In addition, the occurring phase transformations in binary Fe–Mn and Fe–Ni alloys are very similar. Therefore, the knowledge gained here may also be transformed to binary Fe–Ni steels or commercially available alloys.

The ternary Fe–Mn–Pd equilibrium phase diagram is not reported in literature. Hence, the precipitation sequence, observed in the current thesis for the martensitic Fe–Mn–Pd alloys, may assist in the future assessment of the ternary equilibrium phase diagram.

There exists only little literature considering the effect of aging on the corrosion properties of maraging steels. During the course of the current project the influence of isothermal aging time at 500 °C on the corrosion properties of Fe-10Mn and Fe-10Mn-1Pd were studied. However, the results obtained have not been included in this thesis. The degradation behavior was investigated in acid (0.1 M hydrochloric acid, pH= 1) and in more neutral media (buffered, aqueous 0.1 M sodium chloride, pH = 5.3). Considering in the following only Fe-10Mn it was revealed for both test solutions that the degradation rate significantly increased with aging time of the alloys (Fig. 7.1). This behavior was attributed to the formation of revered austenite during aging, which was preferentially attacked during degradation. It is obvious that such a behavior is rather undesirable in structural applications. However, since
aging and thus the associated formation of austenite are important for obtaining strength and toughness in maraging steels, the corrosion behavior of Fe–Mn-based systems clearly needs to be further investigated.

**Fig. 7.1.** Results of degradation tests of Fe and of Fe-10Mn in the SHT state and aged for 30 min, 30 h and 300 h at 500 °C. The mass loss ($\Delta m$) as a function of immersion time in (a) 0.1 M HCl (pH = 1) and (b) aqueous solution containing 0.1 M NaCl buffered with 0.1 M HEPES (pH = 5.3) is displayed. In both test media a significant increase in degradation rate with increasing aging time of the binary Fe–Mn steels is visible. The insert in (a) shows an EBSD scan of Fe-10Mn aged for 300 h at 500 °C revealing the distribution of $\alpha'$-martensite (yellow), $\varepsilon$-martensite (blue) and austenite (red). The inserts 1 and 2 in (b) shows SEM images of cross-sections of samples after 7 days of immersion. A homogeneous corrosion attack is observable for Fe-10Mn in the SHT state (insert 1). However, the corrosion attack preferentially occurred along shallow pits for Fe-10Mn aged for 30 h at 500 °C (indicated by black arrows in insert 2).
8 Appendix
Curriculum vitae

Name: Frank Moszner
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Education

2010-2014 Ph.D. at the Laboratory of Metal Physics and Technology, Department of Materials, ETH Zürich

2007-2009 Master’s degree in Materials Science, ETH Zürich
Master’s thesis at the Laboratory of Metal Physics and Technology on “Influence of thermal cycling and thermo-mechanical processing on Fe-Mn-Pd alloys”

2002-2006 Bachelor’s degree in Materials Science, ETH Zürich
Bachelor’s thesis at the Laboratory of Metal Physics and Technology on “Einfluss der Mikrolegierungselemente Seltene Erden auf die Glasbildungs- und Korrosionseigenschaften im System (Mg₆₇ Ca₅ Zn₂₈)₁₋ₓ Xₓ (X = Ce, Gd, La, Yb, Y)”

1998-2002 Matura, Naturwissenschaftlicher Zweig, Bundesoberstufenrealschule Gymnasium Feldkirch, Austria

Work experience

09/2009-02/2010 Research assistant at the Laboratory of Metal Physics and Technology, ETH Zürich, Processing of metallic glasses and investigation on their glass-forming ability and mechanical properties;

10/2008-04/2009 Research assistant at the Laboratory for Nanometallurgy, ETH Zürich, Mechanical tests on thin tantalum metal films and data analysis.
06-07/2008 Research assistant at the Institute of Korrosion und Werkstoffintegrität, EMPA Dübendorf, “Potential-Mapping via ESCM”

01-06/2008 Master project at the Institute of Korrosion und Werkstoffintegrität, EMPA Dübendorf, “Erzeugung von Nanometer-grossen Strukturen auf Metallsubstraten mittels ESCM (Electrochemical scanning capillary microscope)”

08/2005-09/2007 Master project at the Institute for Surfaces and Interfaces, ETH Zürich, “Self-Assembled Peptide Structures”

10/2006-03/2007 Internship at Siemens AG in the Department of Materials and Microsystems, Munich, Fabrication of oxide coatings, implantation of a test procedure to investigate the adherence of thin oxide films on metal substrates.

05-10/2006 Research assistant at the Institute of Polymer Physics, ETH Zürich, Rheological investigations of polymer melts.

10/2005-01/2006 Semester project at the Institute for Nonmetallic inorganic Materials, ETH Zürich, “Preparation and characterisation of Sr, Mn doped lanthanum chromite perovskite for solid oxide fuel cells”

Publications


Conference contributions


Supervisions of students

• L. Huber (Bachelor’s thesis 2012): 
  Influence of heat treatments of the degradation behavior of martensitic Fe–Mn–Pd alloys

• D. Kokkinis (Master’s project 2011): 
  Thermo-mechanical treatments of biorsobable Fe–Mn–Pd for implant applications

• T. Bachmann (Master’s project 2011): 
  Evaluation of Fe-xMn (x = 35, 50, 65 wt.%) alloys for their use as biodegradable implant material

• C. Baechler (Bachelor’s thesis 2010): 
  Investigation of brittle/ductile behavior of age hardenable biodegradable Fe-xMn-1Pd (x = 10, 12.5, 15 wt.%) alloys
• D. Scherer (Master’s project 2010):
  
  *Hardening behavior of Fe–Mn–Pd and Fe–Mn–Ni alloys*

• F. Reusch and C. Zihlmann (Semester project, 2010):
  
  *Influence of palladium doping on the continuous and isothermal phase transformations of Fe-xMn (x = 5, 10 wt.% alloy)*

• Praktikum IV (2010-2013):
  
  *Experiment: Metallographie M1*

• Praktikum I & II: (2011-2014):
  
  Experiment E-Modul