Precipitation hardening of biodegradable Fe–Mn–Pd alloys

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Abstract

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 {1 0 0} 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. A study of the hardening kinetics shows that the process exhibits all the features characteristic of maraging steels.
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1. Introduction

Interest in biodegradable metallic implant materials has been increasing steadily over the past decade. Besides magnesium, which is already well-established as a 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 in 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 microgalvanic 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 (TWinning Induced Plasticity) effect [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 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 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 techniques were employed to gain microstructural information along the decomposition path on the nanometer scale and to correlate the interaction of 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. Experimental

Two alloys of nominal compositions Fe–10Mn and Fe–10Mn–1Pd (in wt.%, for the alloy composition in at.% see Table 1) were produced from the following raw elements: Fe (Armco), Mn (99.9% pure, Alfa Aesar, Germany) and Pd (99.95% pure, UBS, Switzerland). The elements were melted in a vacuum induction furnace under a 300 mbar argon atmosphere of 99.998% purity and cast into a copper mold. To ensure phase homogeneity, the ingots were encapsulated in quartz tubes under a 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.

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/10 min); SHT followed by aging at 500 °C for 30 min (SHT + 500 °C/30 min); SHT followed by aging at 500 °C for 1800 min (SHT + 500 °C/1800 min). 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 (Tenu-Pol-5, Struers) operated at 10–12 V dc at −40 °C. A solution of 90 vol.% methanol and 10 vol.% perchloric acid served as the electrolyte. The TEM studies were performed using a FEI Tecnai F30 machine operating at 300 keV.

For 3DAP analysis square bars of $0.3 \times 0.3 \times 15 \text{ mm}^3$ 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.% perchloric acid and 75 vol.% 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/1800 min specimens were measured at 80 K because of their brittleness. Data processing was conducted using the IVAS 3.4.1™ software package (Imago Scientific Instruments).

For phase identification, X-ray diffraction (XRD) measurements (PW 1800, Philips) were conducted using Cu K_α ($\lambda = 0.15406$ nm) radiation operating at 45 kV and 40 mA. Quantification of the austenite volume fraction (V_γ) was carried out as proposed by Sha and Guo [17] using the integrated intensity of the (2 2 0) and (2 0 0) γ-phase peaks and the (2 2 0) martensite diffraction line.

Table 1
Nominal compositions in weight (wt.%) and atomic percent (at.%) of Pd-free and Pd-doped alloys.

Alloy	Fe		Mn		Pd	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
Fe–10Mn	90	89.75	10	10.25		
Fe–10Mn–1Pd	89	89.28	10	10.19	1	0.53