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

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Abstract

The embrittlement and de-embrittlement behavior of an Fe–10Mn–1Pd (wt.%) maraging steel upon isothermal aging at 500 °C is 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 alloy and of a binary non-hardenable Fe–10Mn alloy for comparison. 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 states, but there was zero tensile elongation in the intermediate under- and peak-aged regions, where intergranular fracture along the PAGBs occurred. In the brittle peak-aged state a large number of small nanometer-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; 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.

Keywords: Atom probe tomography; Precipitation; Mechanical behavior; Grain boundary embrittlement; Fe–Mn maraging steels

1. Introduction

Maraging steels are a special class of ultra-high-strength steels which harden via the formation of small nanometer-sized intermetallic precipitates. A variety of maraging alloys have been developed; 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 based on metallurgical, electrochemical and toxicological considerations [3], we developed the martensitic alloy Fe–10Mn–1Pd (wt.%) as a prospective biodegradable implant material. The alloy is intended to exhibit an enhanced corrosion rate in physiological environments to overcome the main drawback of biodegradable Fe alloys, i.e. their low degradation rate [3]. High mechanical strength is 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, nanometer-sized precipitates

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rich in Mn and Pd form during isothermal aging at temperatures between 300 and 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 Mn is at least as effective as P 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. Controversy exists 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 have been proposed, including: (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 of spatially resolving 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]. APT can also distinguish between 3-D 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 a 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. Using this approach, we were able to correlate the microstructure and mechanical properties of these alloys.

2. Experimental procedure

Casts of 1 kg of the two alloys with the nominal composition Fe–10Mn and Fe–10Mn–1Pd (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). Cylindrical ingots of 35 mm in diameter were then forged down to a diameter of 12 mm at ~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 ~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 6 s) 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 in 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 (5 min/500 °C), 30 min (30 min/500 °C) and 30 h (30 h/500 °C) were tested. The 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 Kα radiation ($\lambda = 0.15406$ nm) 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.

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]. Fig. 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 scanning electron microscope equipped with a Nordlys EBSD camera operated at 20 kV (Fig. 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. 1c). The sample wedge was transferred to multiple posts. Final sharpening of the tips was performed by annular milling (Fig. 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