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Reverse $\alpha' \rightarrow \gamma$ transformation mechanisms of martensitic Fe–Mn and age-hardenable Fe–Mn–Pd alloys upon fast and slow continuous heating

F. Moszner [a], E. Povoden-Karadeniz [b], S. Pogatscher [a], P.J. Uggowitzer [a], Y. Estrin [c], S.S.A. Gerstl [d], E. Kozeschnik [b,e], J.F. Löffler [a,*]

[a] Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland
[b] Christian Doppler Laboratory for Early Stages of Precipitation, Vienna University of Technology, 1040 Vienna, Austria
[c] Center for Advanced Hybrid Materials, Monash University, Department of Materials Engineering, 3800 Clayton, Australia
[d] Electron Microscopy ETH Zurich (EMEZ), ETH Zurich, 8093 Zurich, Switzerland
[e] Institute of Materials Science and Technology, Vienna University of Technology, 1040 Vienna, Austria

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Abstract

The mechanisms governing the reverse martensite (α') to austenite (γ) 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 the addition of 1 wt.% Pd, respectively. Dilatometric experiments employing heating rates between 0.5 and 200 K min^{-1}, atom-probe tomography measurements on continuously heated specimens and thermo-kinetic simulations were performed. On fast heating (200 K min^{-1}), 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^{-1}, 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.

Keywords: Phase transformation; Martensite-to-austenite transformation; Maraging steels; Computer simulations; Precipitation

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 (α) and austenite (γ). During aging, two important reactions occur: (i) The formation of strengthening nanometer-sized intermetallic precipitates in the martensitic (α') 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

* Corresponding author. Tel.: +41 44 632 2565; fax: +41 44 633 1421.
E-mail address: joerg.loeffler@mat.ethz.ch (J.F. Löffler).

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$\alpha' \rightarrow \gamma$ 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 α and γ 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 $\alpha' \rightarrow \gamma$ 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 $\alpha' \rightarrow \gamma$ 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 γ-growth, and precipitate drag, are considered. The model alloys chosen are characterized by DIL using heating rates 0.5–200 K min^{-1}. 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.

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^{-1}. All measurements were conducted under vacuum ($<10^{-2}$ mbar) to minimize oxidation of the specimens.