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Grain boundary embrittlement by Mn and eutectoid reaction in binary Fe–12Mn steel

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Abstract

The grain boundary embrittlement in a binary Fe–12Mn is due to the grain boundary segregation of Mn. During tempering at 400 °C (higher than the equilibrium eutectoid reaction temperature 247 °C), reverted austenite particles were formed at lath and grain boundaries through the equilibrium reaction of lath martensite to ferrite + austenite. Surprisingly, hydrostatic pressure, which is induced by the transformation of epsilon martensite to austenite during heating at the tempering temperature, resulted in the nonequilibrium eutectoid reaction producing α-Mn precipitates at the interface between lath martensite and the transformed austenite during the tempering. The segregation concentration kinetics of Mn formed a convex profile due to the active grain boundary precipitation of the reverted austenite particles and the α-Mn particles, which act as a sink for the segregated Mn. Finally, the convex segregation profile of Mn corresponded to the concave profile of intergranular fracture strength.

Keywords: Auger electron spectroscopy; Grain boundary embrittlement; Grain boundary segregation; High Mn steel; Eutectoid reaction

1. Introduction

Because Mn produces similar effects to Ni, which is an expensive major alloying element [1,2], it has been considered as a cheaper alternative to Ni. The microstructure in the as-quenched state of binary Fe–Mn steels containing 4–10 wt.% Mn is composed of lath martensite (α') similar to that in 9% Ni cryogenic steels [3–5]. Unfortunately, Fe–Mn steels are very brittle at low temperatures, exhibiting a fracture path along prior austenite grain boundaries, although there is no sign of embrittling second phase particles at the grain boundaries [6–12]. Such intergranular fracture behavior is also observed in steels containing 15–30 wt.% Mn [13–17]. Few systematic investigations of the embrittlement have been performed to date, though some studies suggest that the embrittlement is due to the segregation of N or Mn to prior austenite grain boundaries [18,19], that the embrittlement in steels containing 4–10% Mn is a kind of temper embrittlement [20] or that the intergranular brittleness is inherent to steel containing 12% Mn in the as-quenched condition [21,22]. There has, however, been no decisive evidence for the cause of embrittlement observed in high Mn steels. A fundamental understanding of the embrittlement is therefore important for their application. Meanwhile, Fe–Mn–Ni steels show a remarkable age-hardening response below 500 °C, which is due to the formation of coherent face-centered tetragonal θ-MnNi precipitates in the matrix [23–25]. The alloys also show severe grain boundary embrittlement, even after a short ageing time. It was first reported that the embrittlement in Fe–Mn–Ni steels is due to the segregation of Mn, P and N to prior austenite grain boundaries [25,26]. It has subsequently been shown that the embrittlement is due to the grain boundary segregation of Mn, and the embrittlement to de-embrittlement transition observed during ageing is due to the subsequent desegregation of Mn into the matrix [27,28], which is directly related to the active precipitation reaction of the θ-MnNi particles. On the other hand, it was proposed that the embrittlement to de-embrittlement transition is associ-

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ated with the transition of the face-centered tetragonal θ-MnNi precipitates formed at the prior austenite grain boundaries to austenite particles during aging [29,30].

Concerning the effects of segregants on the cohesion strength of grain boundaries, one opinion is that the segregant occupies a hole in the boundary and locks up metallic bonding electrons, consequently weakening the pre-existing metal–metal bonds [31]. Another opinion is that the segregant replaces a host atom, thus replacing a metal–metal bond by a weaker metal–segregant bond [32]. This latter opinion shows that the Mn as well as impurities may be a strong grain boundary embrittler in iron-based alloys. Mn was originally reported as an embrittler in iron-based alloys [33], and this has been supported by other studies [34,35].

In this study, it is clarified through simple tensile tests in liquid nitrogen and using Auger electron spectroscopy (AES) that the grain boundary embrittlement in high Mn steels is due to the prior austenite grain boundary segregation of Mn. It is shown for the first time that, during tempering at a temperature higher than the equilibrium eutectoid reaction temperature, the nonequilibrium eutectoid reaction producing α-Mn precipitates, which is due to the hydrostatic pressure induced by the transformation of epsilon martensite to austenite (hereafter, γ_t), occurs at the interface of α' and γ_t of a binary Fe–12Mn steel, together with the equilibrium reaction of α' to α+ reverted austenite (hereinafter γ_e). Finally, it is shown that the convex profile of segregated Mn during tempering is directly related to the precipitation of α-Mn and γ_e particles that occurs at the grain boundaries.

2. Experimental

A binary Fe–12Mn steel ingot of 30 kg was prepared using a vacuum induction melting process. The chemical composition of the prepared steel is given in Table 1. The ingot was homogenized at 1200 °C for 3.6 ks and hot-rolled to 20 mm thick plates. The plates were sliced into several sheets with dimensions of 110 mm in total length, 25 mm in width and 1.3 mm in thickness. The sheets were solution-treated in the range of 850–1100 °C in a tube furnace under an argon atmosphere and then water-quenched. Tensile test specimens with dimensions of 93 mm in total length, 25 mm in gauge length, 4 mm in gauge width and 1 mm in thickness were machined from the as-quenched sheets. The specimens were tempered at 400 °C for various times in a salt bath and then water-quenched. Tensile tests were performed at a strain rate of about 1×10^{-3} s^{-1} after holding for 3 min in liquid nitrogen. Phase analyses before and after tempering were carried out using X-ray diffraction (XRD) techniques employing Cu K_α radiation. Phase transformation temperatures were measured in a dilatometer, using cylindrical specimens 3 mm in diameter and 10 mm in length. The heating rate was 7 °C s^{-1} and the cooling rate, by helium gas quenching, was approximately 70 °C s^{-1}. Microscopic analyses were carried out with a conventional scanning electron microscope, a field-emission scanning electron microscope and transmission electron microscopes (TEM). The jet-polishing solution used for the TEM analysis comprised 5% $HClO_4$ + 95% CH_3COOH; additional samples for the TEM analysis were prepared by the focused ion beam method.

Table 1
Chemical composition of the prepared steel (wt.%).

Mn	C	S	P	N	Fe
11.67	0.0014	0.0025	0.0020	0.0002	Bal.

The grain boundary segregation behavior of solutes was investigated by AES. The AES specimens, with dimensions of 16 mm in length, 2.5 mm in width and 1 mm in thickness, that were machined from the tensile-tested specimens were fractured after cooling in liquid nitrogen for about 1.8 ks in a vacuum of about 9×10^{-8} Pa. Peak-to-peak height ratios I/I_{Fe} were obtained from the grain boundary surfaces at about 10 points and averaged. The peaks used were Fe_{703}, P_{120}, C_{275}, N_{389}, O_{510} and Mn_{542}. The primary electron beam voltage was 3 or 10 kV and the electron beam size was about 2 μm.

3. Results and discussion

3.1. Grain boundary segregation of Mn and intergranular brittleness

Changes in average grain size with solution temperature are shown in Fig. 1. Here, the samples were solution-treated first in the range of 850–1100 °C for 3.6 ks, then cooled down to 850 °C, at which they were held for 3.6 ks before being water-quenched. It has been shown from a simple thermodynamic calculation that the grain boundary segregation concentration of solutes in binary alloys increases with increasing grain size [36]. Therefore, the subsequent solution treatment at 850 °C was performed on the samples in Figs. 1–5 in order to show the difference in the grain boundary segregation concentration of solutes (especially, Mn) which results solely from the difference in grain size.

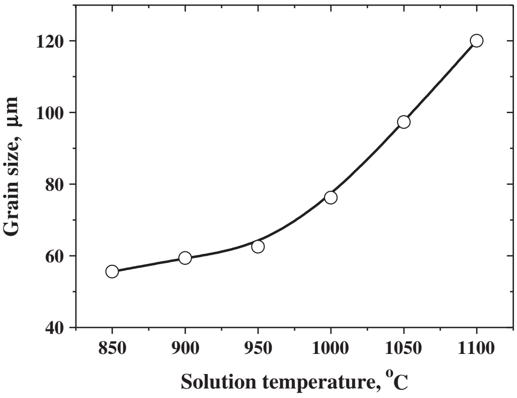

Fig. 1. Change in average grain size with solution temperature.