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The mechanism of order-induced intrinsic embrittlement in a stoichiometric Ni_4Mo alloy by TEM and 3DAP characterization

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Abstract

To illustrate the mechanism of order-induced intrinsic embrittlement in a stoichiometric Ni_4Mo alloy, TEM and 3DAP were employed to investigate the phase separation during ordering in this paper. It showed that the atomic ordering initiated homogeneously, but some oriented ordered domains can grow preferentially later. Therefore, with atomic ordering, the average ordered domain size continues to increase, which improves the yield strength and ultimate strength due to increasing the critical shear stresses. However, except the growth of ordered phase, different phases with enriched molybdenum and depleted molybdenum were formed after ordering. The depleted molybdenum phase gradually reduces the Mo composition, which deteriorates the ultimate strength, and meantime the strength of grain boundary does not enhance, or even weakens. Hence, the atomic ordering induces embrittlement.

Keywords: Nickel alloy; Atomic ordering; Intrinsic embrittlement; Transmission electron microscopy; Three-dimensional atom probe

1. Introduction

Ni-based alloys containing 26–30 wt.% Mo form basis for a number of commercial alloys, e.g., HASTELLOY B-2, which is resistant to reducing media, such as hydrochloric acid [1–3]. However, upon exposure to elevated temperatures in the range of 600–800 °C, these alloys suffer an almost complete loss of room temperature ductility as a result of long-range ordering to Ni_4Mo. We tried to elucidate such embrittlement from environmental embrittlement. But the ductility tested in oxygen atmosphere, which is thought to be immune to the environmental embrittlement, still decreases with atomic ordering, though the brittleness is far from severe than that tested in hydrogen atmosphere [4]. It illustrated that there still exists intrinsic embrittlement induced by atomic ordering.

Some researchers [5–8] have investigated the mechanism of order-induced embrittlement in Ni–Ni_4Mo alloys earlier. They showed that homogeneous matrix ordering only caused a moderate loss of ductility and the fracture mode remained to be transgranular. Discontinuous ordering resulted in molybdenum-depleted zones alongside grain boundaries and therefore resulted in a considerable loss of ductility, intergranular embrittlement due to highly localized deformation in the molybdenum-depleted zones. In addition, they thought that the ordering reaction proceeded homogeneously first, and late a heterogeneous reaction was initiated along the grain boundaries. However, to a stoichiometric Ni_4Mo alloy, the molybdenum-depleted zones formed alongside grain boundaries are some difficult to be understood because the statistical short-range order mode implied homogeneous ordering below the critical temperature T_c, and after nuclei, ordering proceeds by atomic rearrangement within the domains [5]. Further, though the final microstructure seems two-phase, which was analogous to the classical γ/γ' system in terms of precipitate shape, spatial distribution and a minimum distance of separation between γ' precipitates as dictated by the interplay between strain and interfacial energies [9], the two-phase composition was still not evinced because the determination of exact composition of precipitates from EDS data would necessarily involve correction for the matrix overlap. 3-dimensional atom probe (3DAP) can determine the composition of the phases avoiding any uncertainties. Therefore, TEM and 3DAP were employed to investigate the phase separation in a stoichiometric Ni_4Mo alloy in this paper. The aim is to address the question why molybdenum-depleted

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zones and weak grain boundaries are formed after atomic ordering and the mechanism of order-induced embrittlement is also elucidated.

2. Experimental procedure

A stoichiometric Ni_4Mo alloy (analyzed chemical composition is Ni-29.01 wt.% Mo) was prepared and tensile tested as our previous work [4]. For disordering treatment, the specimen was heated at 1066 °C for 30 min and then quenched in water. For ordering treatment, the specimen was annealed at 650 °C for 2 or 7 h and then air-cooled, or annealed at 700 °C for 24 h and then furnace-cooled after disordering. TEM specimens were prepared by mechanical grinding followed by twin-jet electropolishing. Sharp needles used for 3DAP analysis were prepared using standard electropolishing procedures [10]. Atom probe analyses were conducted under ultrahigh vacuum conditions ($<2 \times 10^{-8}$ Pa) at a specimen temperature of 60–100 K.

3. Results

Figs. 1–3 show the typical TEM micrographs and electronic diffractions in Ni_4Mo alloy with different degree of order. In the disordered (α) condition, an appreciable fine structure is not visible except some dislocation in the image (see Fig. 1a). The dislocations are restricted to bands and do not easily form tangles as illustrated in [3]. They are only induced by specimen preparing, illustrating that the critical shear stress in disordered alloy is so low that the dislocation can be easily formed and slip. From the diffraction pattern, the short-range order (SRO) appears (see Fig. 1a′). After ordering at 650 °C/2 h AC, a blurry two-phase region has been formed homogeneously. Though there is essentially no "two-phase" region between an ordered nucleus or microdomain and a disordered matrix as being illustrated in [3], the perpendicular texture can be observed (see Fig. 1b). Some dislocations can also be found and they are mainly separated. From the diffraction pattern, the short-range and long-range order coexists (see Fig. 1b′) and it also shows superlattice spots coming from different oriented domains.

After ordering at 650 °C/7 h AC, the morphology is similar as that of sample ordered at 650 °C/2 h AC. It is homogeneous in all view and even near the grain boundary. The interface of disorder and order is less obscure. The ordered domain has some contrast compared to the disordered domain (Fig. 2a). The dislocation is not found because the critical shear stress increased with atomic ordering [3,11]. From the diffraction pattern, there mainly exhibit two patterns. One pattern is shown in Fig. 2b, which is identical to the section in reciprocal space as [3] and shown all six different orientations for the ordered domain, indicating that the ordered domain is so small that the aperture to diffraction can circle different oriented ordered domains. This area was also shown in the high-resolution TEM image (Fig. 2d), which includes some ordered domains (solid circles) with different orientation and some disordered domains (dashed circles).

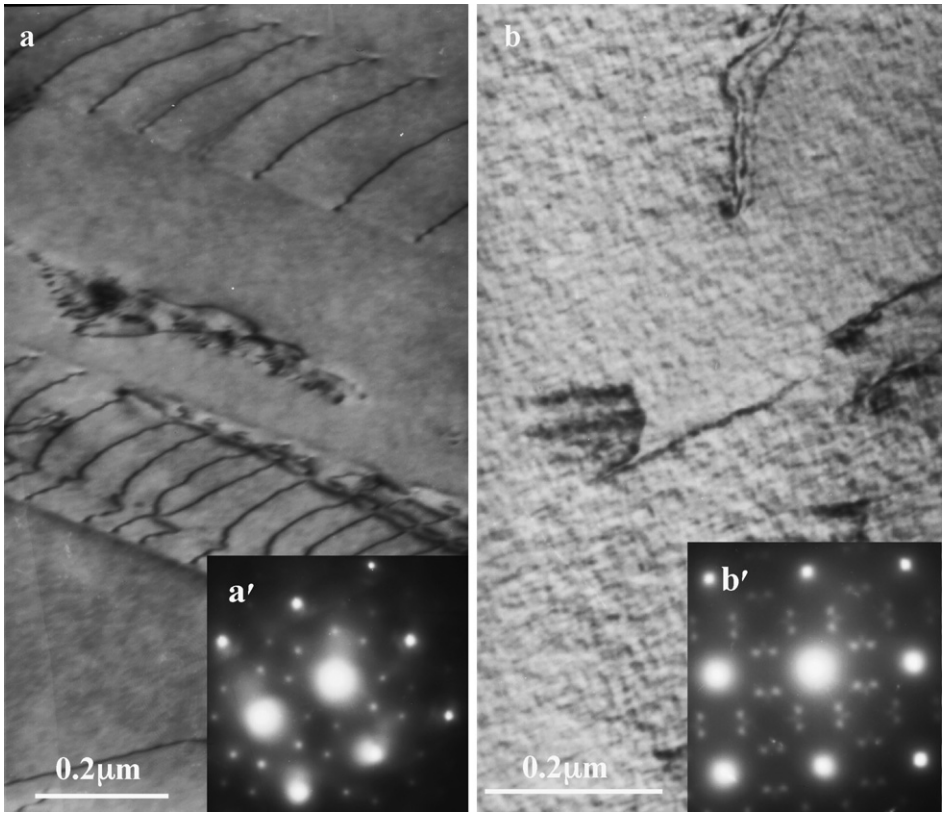

Fig. 1. Microstructure and electron diffraction patterns from a Ni_4Mo alloy (a) disordered, showing [0 0 1] and SRO spots only (a′); (b) ordered at 650 °C/2 h AC, showing [0 0 1] and LRO and SRO spots (b′).