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ScienceDirect
Acta Materialia 55 (2007) 5169–5176
Acta MATERIALIA
www.elsevier.com/locate/actamat

Structure of twin boundaries in Mn-based shape memory alloy: A HRTEM study and the strain energy driving force

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Received 19 December 2006; received in revised form 24 May 2007; accepted 27 May 2007
Available online 23 July 2007

Abstract

The paramagnetic–antiferromagnetic transition and the cubic-tetragonal martensitic transformation in Mn-based alloys occur at the same temperature. The shape memory effect depends on the morphology of twins and the motion of twin boundaries. High-resolution electron microscopy was carried out across the twin boundary. Abnormal lattice distortion was observed and determined to be a twinning dislocation. A model for the defect was established based on the elasticity theory of Eshelby and Khachaturyan. The twinning was found effectively to reduce the strain energy and the introduction of twinning dislocations reduces it further. The strain energy related to these defects was only 2/7 relative to the value in their absence, providing a thermodynamic mechanism for the formation of these twinning dislocations.

Keywords: High-resolution electron microscopy (HREM); Martensitic phase transformation; Shape memory alloys (SMA); Twinning; Dislocation structure

1. Introduction

The magnetic shape memory effect (MSME) of magnetic shape memory alloys (MSMA) has been widely studied since its discovery [1,2]. The mechanism of the effect is attributed to the motion of twin boundaries (TBs) under an external field. These twins are the product of the order–disorder or martensitic phase transformation of these alloys. During the transformation, the symmetry of the cubic high-temperature phase is reduced to the tetragonal or orthogonal phase. However, detailed analysis of the mechanical performance of Ni_2MnGa suggests that the motion of TBs is in fact achieved by the slipping of twinning dislocations (TDs) [3,4]. It appears that the TDs play an important role in the field-induced-strain in these alloys, especially under complex stress conditions. Therefore, a thorough study of the TDs should help to predict the microstructure–property relationship and improve the performance of MSMAs.

The TD concept has long been proposed as an explanation for the curved boundaries observed between lenticular twins [5–7]. Each TD produces a ledge on the perfect twin boundary. If a Burgers circuit is drawn around the TD, the Burgers vector is found to be

$$\mathbf{b} = d\boldsymbol{\varepsilon} \tag{1}$$

where d is the height of the ledge and $\boldsymbol{\varepsilon}$ is the shear strain vector between the twins. The TD shares many properties with ordinary dislocations except that the TD can only slip along the TB. Since the boundary of the lenticular twin can be regarded as consisting of the loops of TDs, the shape of the twins is closely related to the distribution of TDs and can be calculated from the theory of dislocation piling.

The relationship between the density of TDs, D, and the angle of deviation of the TB from the twinning plane, θ, can be written as

$$D = \frac{a}{d}\tan\theta$$

where a refers to the unit-cell spacing.

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1359-6454/$30.00
doi:10.1016/j.actamat.2007.05.050

Apparently, such dislocations are a kind of coherent dislocation, as shown by the schematic drawing of an edge-type TD in a face-centered tetragonal (fct) structure in Fig. 1. Zhu [8], using high-resolution transmission electron microscopy (HRTEM), observed TDs directly on the (1 1 0) twin boundary in the high-T_C superconductor YBCO. In YBCO and most alloys with fct structure, the tetragonality, $|1-c/a|$, is close to or less than 0.05. Hence, the length of the shear strain vector ε is also small. According to Eq. (1), the TD Burgers vector is much less than the dimension of the unit-cell. Thus it is believed that TDs do not produce diffraction contrast and HRTEM is the only possible method to investigate these defects.

In this paper, HRTEM is used to study TDs in γ-$Mn_{85}Fe_{10}Cu_5$ alloy, which is a typical antiferromagnetic (AF) shape memory alloy with fct crystallographic structure at room temperature [9–11]. Previous study has found its twin boundary to be {1 0 1} and there must be TDs on the TBs since the TBs are not parallel [12]. From the softening of the shear elastic constant, $C' = (C_{11} - C_{12})/2$ [13–15], and the similarity of microstructure morphology between the alloy and InTl alloy [16,17], it can be supposed that the tetragonal distortion is mainly caused by a martensitic transformation (MT), which is also called the "double-shear mechanism" [18]. However, this conjecture does not contradict the assumption that the cubic-tetragonal crystal lattice rearrangement is a result of antiferromagnetic ordering, as will be discussed in detail in the following section. Since the YBCO twinning is caused by the ordering of oxygen atoms, the difference in twinning mechanisms must lead to a difference between the alloy and YBCO in the atomic-scale configuration near the TD. In fact, most MSMAs, such as Ni_2MnGa and FePd, undergo softening of C' and MT to produce the tetragonal twin structure. Therefore, it should be possible to extend the results and conclusions of the present study to all alloys of this type.

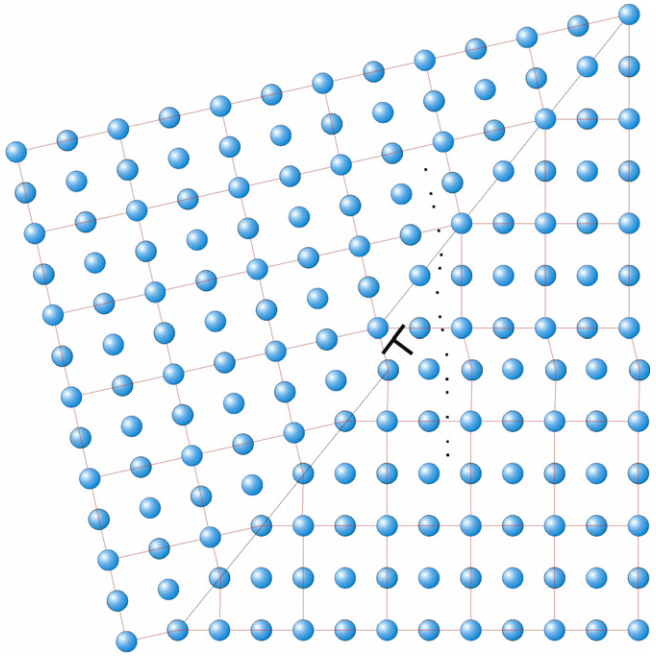

Fig. 1. Atomic model of a twinning dislocation in a tetragonal lattice. Its effect is to produce a step in the twin boundary.

Conversely, since TDs exist in so many different kinds of materials, there must be some intrinsic origin that produces such defects. In some previous studies, the existence of TDs is assumed in advance and the problem is not quantitatively discussed. The elastic strain energy of the MT mainly determines the morphology. Thus, the curved TBs produced by TDs could be the result of minimization of strain energy. To confirm this possibility, the elastic energy of twin structures with and without TDs is calculated and compared for both elastic isotropic and anisotropic media. Thus, it is determined how TDs can assist in reducing the elastic energy associated with the MT.

2. Experimental

The $Mn_{85.5}Fe_{9.5}Cu_5$ (atom percent) alloy was prepared by medium-frequency induction melting of pure manganese and iron under an argon atmosphere. Copper (5 at.%) was added to stabilize the γ phase, hindering the γ–α transformation upon quenching [19]. The ingot was annealed at 1233 K for 12 h and quenched in water. The annealing treatment enables a complete martensitic structure at room temperature. The experimental TEM investigations of the microstructure were performed using a JEM-2100F(FEG) operated at 200 kV. Thin foils were prepared by mechanically grinding foil cut from the ingot to ~0.1 mm in thickness, followed by electropolishing using a twin-jet method, at around −30 °C in an electrolyte of 3% perchloric acid ethanol solution. The specimen was ion-milled just before being placed into the electron microscope to minimize oxidation.

3. Results

3.1. Effect of oxidation on the HRTEM image

Despite the specimen being cleaned by ion milling, it was inevitably oxidized when observed under the electron microscope. Direct evidence for the existence and type of oxide was provided by the selected-area electron diffraction (SAED) pattern of different zone axes from the same specimen region, as shown in Fig. 2. The oxide was easily indexed as MnO, which has an NaCl-type structure with oxygen atoms embedded in the octahedral interspace between fct Mn cells.

From the SAED patterns, it was found that the scattering intensity of the oxide film was fairly strong and the interactions of the oxide could thus have a negative effect on the HRTEM image. The moiré fringes observed in two perpendicular directions in the micrograph (see Fig. 3) are due to overlap of the sample matrix with the oxide film, because the modulation period is a common