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Nucleation and growth of hierarchical martensite in epitaxial shape memory films

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ABSTRACT

Shape memory alloys often show a complex hierarchical morphology in the martensitic state. To understand the formation of this twin-within-twins microstructure, we examine epitaxial Ni-Mn-Ga films as a model system. In-situ scanning electron microscopy experiments show beautiful complex twinning patterns with a number of different mesoscopic and macroscopic twin boundaries between already twinned regions. We explain the appearance and geometry of these patterns by constructing an internally twinned martensitic nucleus, which can take the shape of a diamond or a parallelogram, within the basic phenomenological theory of martensite. These nucleus contains already the seeds of different possible mesoscopic twin boundaries. Nucleation and growth of these nuclei determines the creation of the hierarchical space-filling martensitic microstructure. This is in contrast to previous approaches to explain a hierarchical martensitic microstructure. This new picture of creation and anisotropic, well-oriented growth of twinned martensitic nuclei explains the morphology and exact geometrical features of our experimentally observed twins-within-twins microstructure on the meso- and macroscopic scale.

1. Introduction

Martensitic microstructures often exhibit a hierarchical twin-within-twins microstructure that displays a corresponding hierarchy of typical lengths, which often span several orders of magnitude. While such hierarchy can exhibit beautiful patterns (e.g. Fig. 1), this microstructure and the different types of twin boundaries are critical for several functional properties of martensitic materials. One example is provided by Ni-Mn-Ga magnetic shape memory alloys [1] where the presence of either type I or type II twin boundaries within the martensitic microstructure results in twinning stresses [2] and mobilities differing [3] by an order of magnitude. Another key functional property depending on the microstructure is the transformation hysteresis loss, which must be as low as possible for magnetocaloric and elastocaloric refrigeration [4].

To understand the formation of this hierarchical microstructure, we used epitaxial Ni-Mn-Ga films as a model system. All types of Ni-Mn-X ($X = Ga$, In, Sn, Al) films show a characteristic hierarchical microstructure [5–12] and are of scientific and technological interest due to their magnetic shape memory [13–15], magnetocaloric [10,12,16,17] and multicaloric [18] properties. The absence of large angle grain boundaries makes epitaxial films similar to single crystals, but easier to grow and with a well-defined and clean surface right after deposition. The high surface-to-volume ratio of a film allows taking examinations of the surface as representative for most of the sample. Moreover, the rigid boundary condition to the substrate is beneficial for analysis since it provides a fixed reference frame. The high aspect ratio of a film gives a good statistical representation of nucleation during a martensitic transformation as the thick, rigid substrate elastically decouples most of the thin film from itself.

In this work, we will demonstrate that the shape of the nucleus

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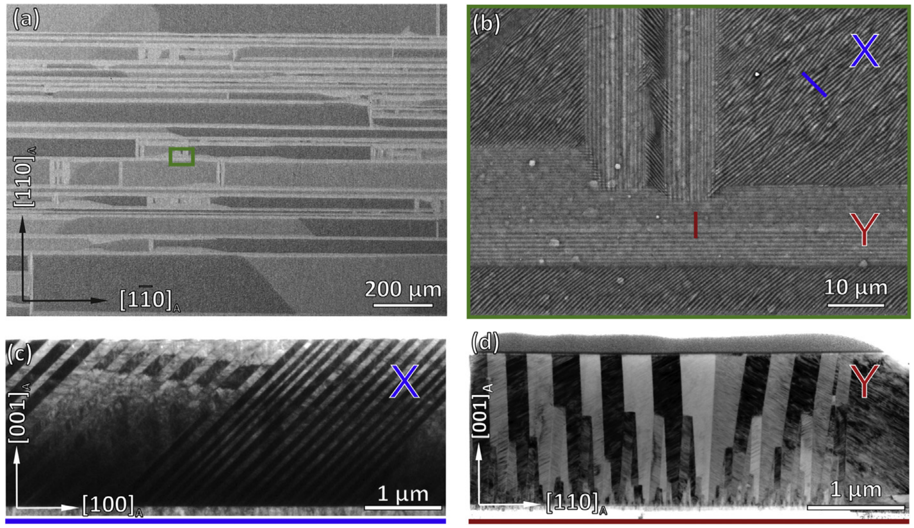

Fig. 1. Hierarchical twin-within-twins martensitic microstructure. (a) SEM micrograph (backscattered electron contrast) of an epitaxial Ni-Mn-Ga film in the martensitic state at room temperature. The surface has a complex yet regular microstructure, dominated by macrotwin boundaries. (b) A magnification at the area marked in green in (a) shows the characteristics of two microstructures called type X and type Y. All contrast stems from mesoscopic twin boundaries due to topography (type X) and variant orientation (both types).(c) is a TEM cross-section of the film in the region marked by the blue line in (b) of type X, (d) of type Y marked by the red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is decisive for the formation of a hierarchical microstructure. For this we first describe briefly the final microstructure. Then we introduce two related geometrical shapes of nuclei: A diamond and a parallelogram. Finally, we present in-situ experiments, which illustrate how these nuclei form the hierarchical microstructure. Before coming to the results, we summarize the theoretical concepts and the state of art.

1.1. Phenomenological theory of martensite

A common concept to describe the microstructure of martensites is the phenomenological theory of martensite, which was developed by Wechsler, Lieberman and Read [19], and independently by Bowles and MacKenzie [20]. In this continuum description of crystallography it is assumed that all stress occurring during a symmetry-breaking phase transition is concentrated at the phase interface, and is minimized by introducing twin boundaries in the martensite. An accurate description of the microstructure after the phase transition is often achieved by postulating that all twin boundaries and phase interfaces have to be invariant planes under the transformation. Modern descriptions of the formalism were published e.g. by Bhattacharya [21] and Pitteri and Zanzotto [22]. The boundary conditions of invariant interfaces can be written in a matrix formalism. As input parameters, only the symmetry and the lattice constants of both phases are required. The geometric constraint at the boundary conditions yields the fraction of martensite twin variants along an invariant plane forming the phase boundary in addition to the relative orientation of both phases, all martensitic variants and all interfaces. The phase boundaries are planar and called habit planes. Due to its continuum character, the theory cannot provide the absolute size or spatial distribution of the microstructural features or information about the transformation path, but the absence of a scale makes it useful to describe twin-within-twin microstructures of higher order. Here we apply this theory to the transition from cubic austenite to a monoclinic 14M martensite as appropriate for the Ni-Mn-Ga alloy film used for our experiments. For a descriptive understanding of the complete paper it is sufficient to keep in mind we consider that habit planes are formed by a combination of nanotwinning and related *a*-*b*-twinning in the modulated phase (see Ref. [23] for a recent discussion). The calculation of the habit plane for this particular system is described in detail elsewhere [24]. They are close to $\{110\}_A$-planes, but differ by a few degrees.

1.2. Modulation and adaptive nanotwinning

The modulations of martensite can be considered a part of the hierarchical martensitic microstructure: According to the classical concepts of martensite, the twinning periodicity is a result of total energy minimization, which contains the elastic (volume) energy and the twin boundary energy. Following the concept of adaptive martensite [25] in case of a huge elastic and low twin boundary energy the twin boundary periodicity can be reduced to the nanoscale in order to adapt at the phase boundary to the austenite. Accordingly modulated structures can be considered as nanotwinned. The adaptive concept was also successfully applied for the particular 14M modulation in Ni-Mn-Ga examined here [5,26,27]. Recently also the regular arrangement of nanotwins within a modulation and the formation of *a*-*b*-twin boundaries has been explained by an interaction energy between nanotwins [23]. Thus a modulated structure can be considered as the first generation of twinning within a hierarchical martensitic microstructure.

However, there are competing explanations of modulated martensite and throughout the rest of this paper we will use the 14M unit cell as starting point to analyze the appearance of the hierarchical martensitic microstructure at the meso- and macroscale. In other words, this manuscript is not directly discussing the shortest length scale of twinning at the nanoscale. The construction of the modulated phases by nanotwinning is discussed elsewhere [23,24,26,28].

1.3. Hierarchical martensitic microstructures

Although there are several experimental observations of twin-within-twin microstructures in various martensites [29–33] and in particular in martensitic Heusler alloys [5–12,34–37], there are just a few theoretical concepts explaining the entire microstructure. Phenomenological theory of martensite allows to construct