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Elemental segregation to twin boundaries in a MnAl ferromagnetic Heusler alloy

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ABSTRACT

Electron microscopy and atom probe tomography were combined to investigate the crystallography and chemistry of a single twin boundary (TB) in a rare-earth-free ferromagnetic MnAl Heusler alloy. The results establish a significant segregation of Mn along the twin boundaries. An enrichment of approx. ~8 at.% Mn was measured along the twin boundary with a confined depletion outside the twin boundary, suggesting short range solute diffusion occurring during massive transformation.

The low-cost, binary Heusler $Mn_{55}Al_{45}$ intermetallic exhibits ferromagnetic properties [1] and is a promising rare-earth-free magnetic material that shows superior performance compared to ferrites [2–4]. The stoichiometric $Mn_{55}Al_{45}$ is an ordered compound that adopts a $L1_0$ structure (*P*4/*mmm* space group). This compound, identified as 'τ', is a metastable phase that evolves by suppressing the formation of equilibrium β-Mn (cubic) and γ_2 (Al_8Mn_5, rhombohedral) phases from the high temperature hexagonal-close packed (hcp) ε phase [1, 5]. The equilibrium phases are non-magnetic and their presence, even in trace fractions in the alloy, deteriorates the magnetic properties. The formation of these equilibrium phases can also be avoided either during controlled melt solidification [6–8] and/or by suppressing the τ phase decomposition [9, 10]. Recently, Mix et al. [10] reported that addition of Ga (5 to 9 at.%), replacing Al, makes the τ phase thermodynamically stable up to 700 °C with improved magnetic properties. Otherwise, τ decomposes into the β-Mn and γ_2 phases on prolonging heat treatment even at 450 °C.

Early reports of the ε-to-τ phase transformation indicated that the transformation is martensitic in nature [11, 12], while later investigations revealed a massive mode of transformation involving diffusional nucleation and growth phenomena [13–17]. In this mode, τ forms at grain boundaries within hcp-ε during cooling or isothermal annealing, and the moving interphase boundary of τ migrates, thereby consuming the ε grain with no specific crystallographic orientation relationship [18, 19]. During growth, the internal structure of τ develops lattice defects such as micro-twins, antiphase boundaries and dislocations [19, 20]. This is attributed to growth misplacements at the interphase boundary during its migration [19, 21, 22]. This defective structure is shown to influence the magnetic hysteresis of the ferromagnetic τ phase alloy [23, 24]. Recent investigations by micromagnetic simulations in this alloy reveal that twins act as domain wall nucleation and pinning sites and are thus responsible for reducing the external magnetic field required to nucleate these domain walls [25]. The alloy studied here has a high density of twins and is shown to have indeed a reduced maximum energy density product, $(BH)_{max}$, with ≈5% of the theoretical limit, 112 kJ/m^3, where B is the magnetic flux density and H is the magnetic field. Further processing such as extrusion and heat treatment can improve $(BH)_{max}$ through removing these defects from the microstructure [25].

Here, we present evidence that the twinning process involves a significant segregation of Mn along the twin boundaries. An approach combining transmission electron microscopy (TEM) and atom probe tomography (APT) [26] was used to reveal both crystallography and local composition of twins in a MnAl ferromagnetic Heusler alloy.

An ingot of nominal composition Mn - 45 at.% Al (constituent elements, 99.9% purity, Alfa Aesar) was synthesized by conventional vacuum arc-melting in high purity (99.999%) argon using a chilled water cooled copper hearth and a tungsten electrode. Initially, the mixed constituents are continuously heated at a slow rate up to the alloy's melting temperature followed by cooling for around 30 s under vacuum. This cycle was repeated at least three times and the overall composition progressively adjusted to compensate for the evaporation loss after each melting by addition of approx. 1.5 at.% Mn. This procedure was optimized such that no equilibrium nonmagnetic phases are formed. The ingot was subsequently heat treated at 1100 °C for 10 h in the single ε

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phase regime followed by water quenching to retain ε at room temperature. The metastable τ is obtained by intermediate annealing at 450 °C for 5 h. To locate the twinned region and reveal the microstructure of the τ phase, a Zeiss Merlin scanning electron microscope (SEM, Carl Zeiss SMT, AG, Germany) equipped with a Gemini-type field emission gun electron column was used. The operating accelerated voltage of 30 kV with 4 nA probe current was applied. Additionally, the twinned region was confirmed by electron backscattered diffraction (EBSD) mapping that was carried out in JEOL-6500F field-emission SEM operated at 15 kV. The analysis of the EBSD data was carried out using the TSL OIM 6.2 software. The regions of interest were marked and site-specific atom probe specimens for correlative TEM and APT investigation were fabricated using a dual beam SEM/focused-ion-beam (FIB) instrument (FEI Helios Nanolab 600) with an in-situ lift-out procedure outlined in reference [27, 28]. The regions with the twinned structure were positioned and welded, by Pt deposition, on electropolished tips of a halved TEM Mo-grid mounted in a special correlative holder [29]. These were sharpened by FIB milling followed by a cleaning procedure at 5 kV and 8 pA current to remove damaged regions induced by Ga ion during high-energy (30 kV) milling. Diffraction studies by TEM on the APT tip was carried out using a Phillips CM-20 instrument operated at 200 kV. Atomic-scale compositional analysis was conducted by performing APT with the LEAP™ 5000XS instrument (Cameca Instruments). Laser pulsing mode was applied at a pulse repetition rate of 200 kHz and a pulse energy of 40 pJ. The specimen's base temperature was kept at 40 K and the target detection rate was set to be 5 ions detected every 1000 pulses. Data analysis was performed using the software package IVAS 3.8.0.

Fig. 1(a) shows an X-ray diffraction pattern for the sample annealed at 450 °C for 5 h. Diffractions peaks observed only pertain to the $L1_0$ ordered structure for the ferromagnetic τ phase with lattice parameters *a* and *b* as 2.77 Å and 3.54 Å respectively. No other diffraction peaks are present. Fig. 1(b) shows a backscattered electron (BSE) micrograph for the annealed sample. A high density of micro-twins is readily visible. EBSD mapping, as shown in Fig. 1(c), further confirmed the presence of these twins. The measured misorientation across the twin boundaries (A to B in inset Fig. 1(d)) is 75.6° as shown in the plot in Fig. 1(e). The misorientation angle corresponds to true twins and is consistent with the earlier report that these represent a major fraction of twins in MnAl alloy [23]. These micro-twins were of varying thickness ranging from ~10 nm to approx. 2 μm.

To confirm the origin of these twins, we present a BSE image in Fig. 2 (a) for the sample annealed at 450 °C for 15 min. It shows a ε phase grain boundary where τ nucleated as the starting stage of ε-to-τ phase transformation. The formation of micro-twins just behind the migrating interface boundary inside the massively transformed τ region is clearly revealed.

APT specimens were extracted at an inclined orientation as shown by the dashed red triangle in Fig. 2(a), to increase the probability for capturing at least one twin boundary. Fig. 2(b) shows a bright field (BF) image of an APT specimen in which twins appear with a dark contrast across the entire specimen. Fig. 2(c) shows the selected area diffraction (SAD) pattern from the region indicated by the white circle in Fig. 2(b). The diffraction pattern could be indexed as [101] zone axis corresponding to the τ phase. In addition to the matrix spots, we also

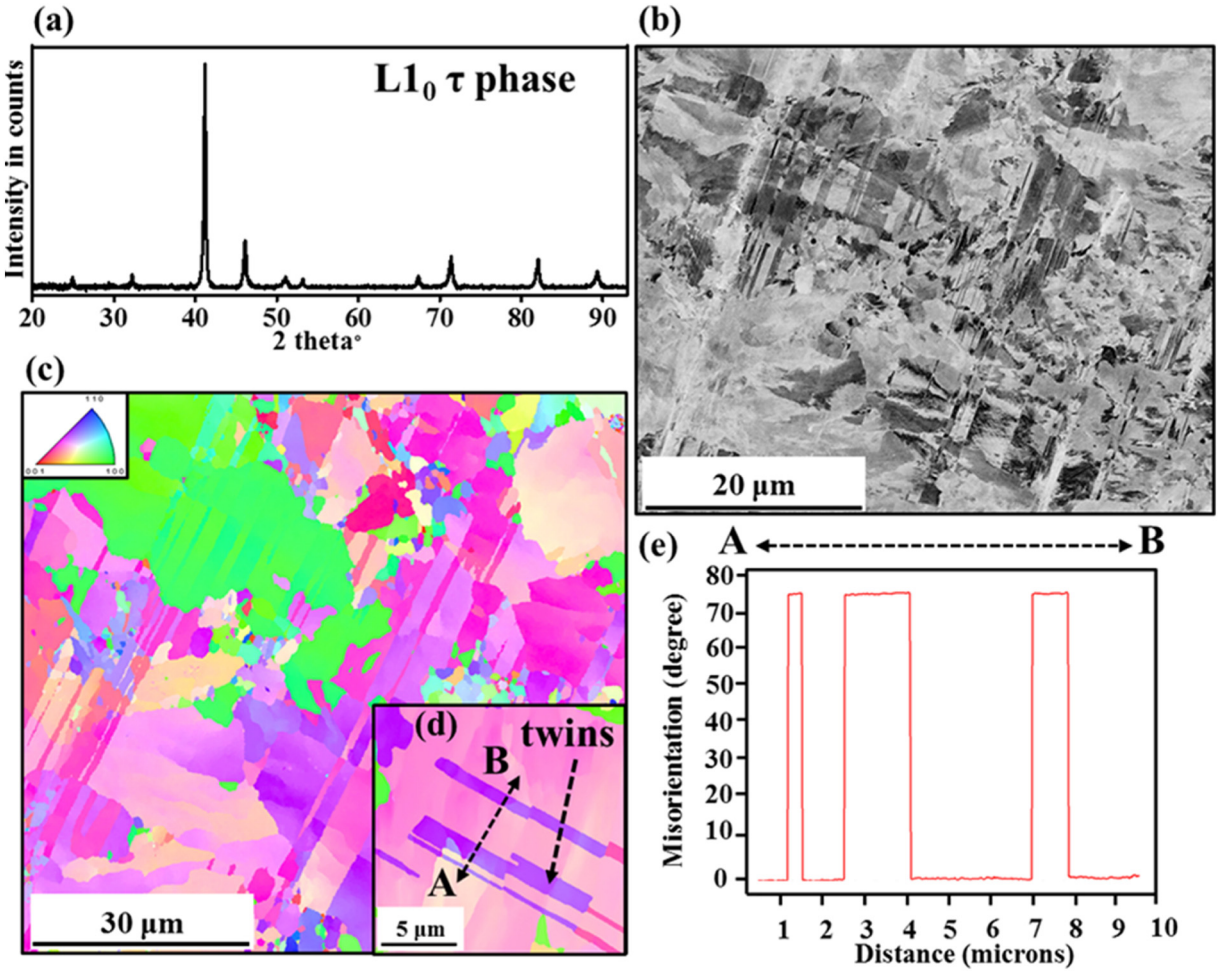

Fig. 1. (a) X-ray diffraction evidence for complete τ phase in the sample annealed at 450 °C for 5 h. (b) Backscattered electron (BSE) image for τ phase microstructure showing the presence of high density of micro-twins. (c) Electron backscattered diffraction (EBSD) map of a τ phase area showing evidence of micro-twins in the microstructure. (d) EBSD map for few micro-twins and (e) the misorientation plot across the twin boundaries (along AB).