Scripta Materialia 126 (2017) 20–23

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

On the effect of titanium on quenching sensitivity and pseudoelastic response in Fe-Mn-Al-Ni-base shape memory alloy

M. Vollmer [a,*], P. Krooß [a], I. Karaman [b], T. Niendorf [a]

[a] Universität Kassel, Institut für Werkstofftechnik (Materials Engineering), 34125 Kassel, Germany
[b] Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA

ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form 28 July 2016
Accepted 1 August 2016
Available online xxxx

Keywords:
Martensitic phase transformation
Abnormal grain growth
Superelasticity
Precipitates
FeMnAlNiTi

ABSTRACT

In the present study, the effect of Ti addition on the microstructure evolution and pseudoelastic properties of a Fe-Mn-Al-Ni shape memory alloy were investigated. By replacing 1.5 at.% Al by Ti in Fe-Mn-Al-Ni, it was possible to strongly hamper the formation of the ductile, non-transforming γ-phase, which is detrimental to the pseudoelastic performance. Single crystalline samples were fabricated via abnormal grain growth. Following aging treatment at 250 °C compression testing at various testing temperatures was conducted up to 10.5% strain using a near ⟨102⟩ oriented single crystal. A low Clausius-Clapeyron slope and good pseudoelastic properties were found.

Due to relative low costs for alloying elements and good workability compared to conventional shape memory alloys (SMAs), iron based SMAs have attracted considerable attention in the last decade [1–10]. However, some of the main drawbacks hindering widespread application of firstly developed alloys are the high discrepancy between theoretical and experimental transformation strains, very low transformation temperatures, and the non-thermoelastic nature of martensitic transformation. In 2010 Tanaka et al. [11] reported a Fe-Ni-Co-Al based alloy system undergoing a thermoelastic transformation between a γ parent phase and an α′ product phase resulting in large reversible strains up to 13%. One year later, in 2011, Omori et al. [12] discovered the Fe-Mn-Al-Ni alloy, which is characterized by an unusual thermoelastic transformation between an α bcc parent phase and a γ′ fcc product phase exhibiting a low Clausius-Clapeyron (CC) slope of 0.53 MPa/°C over a wide temperature range between −196 °C and 240 °C. They were able to show excellent pseudoelasticity with more than 5% strain in the polycrystalline state with a relative grain size exceeding the cross section of the sample. The grain size was accomplished by a cyclic heat treatment, resulting in abnormal grain growth (AGG) [12,13]. Since then a considerable number of studies focused on the single crystal behavior [14–16], the effect of thermo-mechanical processing [17–20], cyclic degradation [21] and processing by additive manufacturing [22] of Fe-Mn-Al-Ni SMAs.

Coherent nano-sized precipitates, i.e. $L1_2$ ordered γ′-$(Ni,Fe,Co)_3(Al,Ta)$ phase in the Fe-Ni-Co-Al based alloys [11] and B2 ordered β-(NiAl) phase in Fe-Mn-Al-Ni [12], are crucially needed in these new Fe-based SMAs to change the martensitic transformation character from non-thermoelastic to thermoelastic [11,12,17]. Before, it was shown that nano-sized B1 ordered NbC precipitates were able to improve the functionality of Fe-Mn-Si based SMAs, due to the introduction of preferential nucleation sites for the stress-induced martensitic transformation and internal stress fields for reverse transformation [23–25]. In addition to the significant impact of size, shape and volume fraction of the finely dispersed precipitates on the pseudoelastic behavior, a strong correlation between the formation of precipitates and hardness values of the materials has also been demonstrated [15,26–28].

In recent work it was shown that following solution heat treatment, precise control of the γ-phase formation by variation of cooling conditions in Fe-Mn-Al-Ni is crucial in order to prevent grain boundary cracking [19]. However, the γ-phase is not desirable for attaining good pseudoelasticity [19], as this phase is non-transforming and, thus, dissipates the elastic strain energy associated with martensitic transformation in the matrix by non-reversible plastic deformation. The evolution of γ-phase is extremely rapid. A transfer time of parts from the furnace to the quenching medium of 5 s was sufficient to promote a fraction of about 40% of γ-phase [19]. Consequently, rapid chemical decomposition being responsible for γ-phase evolution during quenching of these alloys is a significant drawback concerning practical applications as this limits the sample cross sections that can be free of detrimental non-transforming phase eventually showing perfect pseudoelasticity.

With this background, the current study focuses on the addition of a small amount (1.5 at.%) of titanium, which is known to be an α-phase stabilizer [29], to the Fe-Mn-Al-Ni alloy in order to slow down γ-phase formation during quenching. In order to characterize the deformability of the alloy, an oligocrystalline structured, i.e. bamboo structured, tensile sample was tested at 20 °C. Vickers microhardness

* Corresponding author.
E-mail address: vollmer@uni-kassel.de (M. Vollmer).

http://dx.doi.org/10.1016/j.scriptamat.2016.08.002
1359-6462/

values were measured following various aging times and temperatures. Heat treatments were conducted in order to induce nano-sized precipitates, known to be crucial for thermoelastic martensitic transformation. Thermo-mechanical testing was carried out in the temperature range from −150 °C up to 20 °C using a near ⟨102⟩ oriented single crystalline compression sample grown utilizing AGG in order to determine the pseudoelastic performance of the alloy.

Ingots with a chemical composition of Fe-34.0%Mn-15.0%Al-7.5%Ni-1.5%Ti (at.%) and Fe-34.0%Mn-16.5%Al-7.5%Ni (at.%) used in this study were produced by vacuum induction melting using commercially pure metals. Small samples with gauge section of 18 mm × 1.6 mm × 1.5 mm from both alloys and compression samples with dimensions of 3 mm × 3 mm × 6 mm from Fe-Mn-Al-Ni-Ti were electro discharge machined. For heat treatment the samples were sealed in quartz tubes under argon atmosphere. In order to investigate the γ-phase formation during slow cooling, Fe-Mn-Al-Ni and Fe-Mn-Al-Ni-Ti tensile samples were solution treated at 1225 °C for 1 h to ensure a homogenous α structure and subsequently taken out of the furnace and cooled in ambient atmosphere to room temperature within 240 s (hereafter referred to air cooled). Microstructual analyses were conducted using a Keyence digital VH-100 optical microscope and a scanning electron microscope (SEM) operated at 20 kV equipped with a backscattered electron detector (BSE detector). Samples for optical microscopy were mechanically polished to 1 μm grit size and etched for 1 s using a solution of 3% nitric acid diluted in alcohol. Afterwards the Fe-Mn-Al-Ni-Ti sample was additional vibration-polished using colloidal SiO_2 suspension with 0.05 μm particle size to obtain surface quality needed for BSE imaging.

In order to characterize the ductility of the grain boundaries, a tensile test was performed using a bamboo structured Fe-Mn-Al-Ni-Ti tensile sample. The sample was heat treated at 1225 °C for 30 min, cooled down with a cooling rate of 10 °C/min to 900 °C, held for 15 min at 900 °C and finally heated up with a heating rate of 10 °C/min for a solution treatment at 1225 °C for 1 h followed by air cooling. Afterwards, the sample was mechanically polished to 5 μm grit size and the tensile test was performed using a MTS servo-hydraulic testing system in displacement control at a rate of 5 μm/s. The strain was measured by an extensometer directly attached to the gauge length. Afterwards, microstructural analyses were carried out using the optical microscope mentioned above.

Samples for aging studies and pseudoelastic testing were cyclically heat treated between 1225 °C and 900 °C for three times (holding times and cooling/heating rates as mentioned above) and finally solution treated at 1225 °C for 1 h followed by air cooling. Afterwards, samples were mechanically polished to 5 μm grit size and vibration-polished.

In order to measure the increase of hardness of the alloy due to aging, Vickers microhardness values were determined employing a force of 9.8 N for the bamboo structured sample shown in the inset of Fig. 2. The sample was wire cut and one sample was aged at 200 °C for 10 h, whereas another sample was aged at 250 °C for different durations to form coherent nano-precipitates. Electron-backscatter diffraction (EBSD) analyses were conducted to evaluate the grain orientations using the SEM mentioned above operated at 20 kV.

For characterization of pseudoelastic performance a near ⟨102⟩ orientated single crystalline compression sample, obtained via AGG, was tested in the pseudoelastic regime at different temperatures (−150 °C, −90 °C, −40 °C and 20 °C) using the MTS servo-hydraulic testing system mentioned above. A cooling chamber equipped with a liquid nitrogen cooling system was used to allow for cryogenic mechanical testing. Temperatures have been measured by using a thermocouple mounted within the chamber. Tests were carried out in displacement control at a rate of 5 μm/s up to 1.5% strain measured by an extensometer directly attached to the compression grips. Finally, an incremental strain test at 20 °C was performed up to a maximum strain of 10.5%.

Fig. 1 shows the optical micrographs of air cooled samples following a solution treatment at 1225 °C for 1 h for Fe-Mn-Al-Ni (Fig. 1a) and Fe-Mn-Al-Ni-Ti (Fig. 1b). As already reported in [19] non-rapid cooling of Fe-Mn-Al-Ni leads to second phase formation mainly at the grain boundaries with a serrated interface, due to a fast short-range diffusion of Mn and Al stabilizing the γ-phase. The same phenomena are shown in Fig. 1a. This microstructural condition is detrimental to the pseudoelastic performance in two ways:

(i) γ-Phase is a non-transforming phase, reducing the volume fraction of the phase showing a reversible phase transformation.
(ii) The serrated γ - α interfaces represent additional constraints with respect to the recoverability of the martensitic transformation.

On the other hand, quenching in cold water leads to crack formation along the grain boundaries [19]. A thin layer of γ-phase at the grain boundaries is able to prevent intergranular cracking during quenching without notably affecting the pseudoelastic performance [19]. However, in Fe-Mn-Al-Ni, the cooling rates need to be extremely high to achieve this, which is not desirable in practical applications where relatively large cross sections are needed. Therefore, controlling the quenching sensitivity of the alloy is crucial in order to obtain an acceptable pseudoelastic performance in large scale components.

From Fig. 1b it is obvious that the γ-phase formation during air cooling in Fe-Mn-Al-Ni-Ti is strongly hampered, without any observable crack formation along the grain boundaries. Moreover, a thin layer of second phase is seen at the grain boundaries (inset of Fig. 1b). Consequently, the addition of 1.5 at.% Titanium seems to significantly slow down the decomposition during air cooling. In order to characterize the ductility of the grain boundaries during martensitic transformation, a tensile test was performed on a bamboo structured non-aged Fe-Mn-Al-Ni-Ti sample. It is well known that a large relative grain size is required for good performance in Fe-Mn-Al-Ni alloys due to incompatibility across grain boundaries upon martensitic transformation as a consequence of the lack of sufficient transformation systems to satisfy the compatibility [12,14,18]. Omori et al. [13] recently reported a new

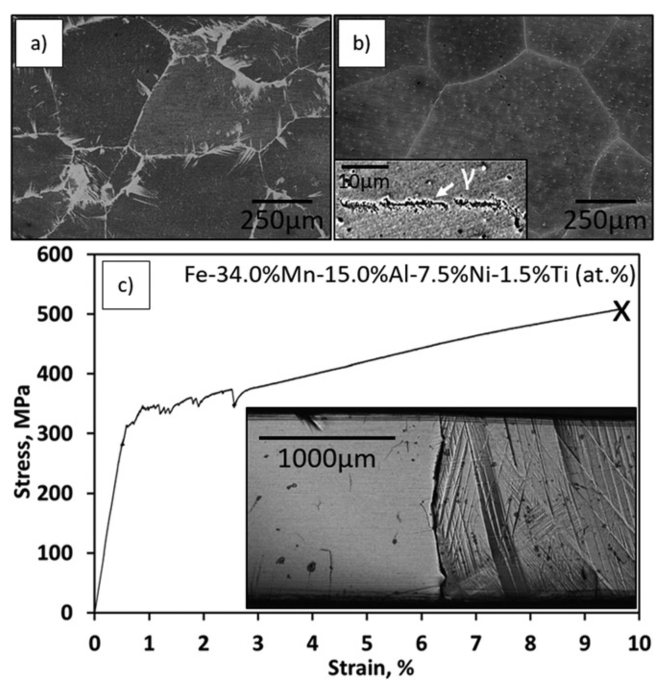

Fig. 1. Optical micrographs of air cooled samples after solution treatment at 1225 °C for 1 h for (a) Fe-34.0%Mn-16.5%Al-7.5%Ni (at.%) and (b) Fe-34.0%Mn-15.0%Al-7.5%Ni-1.5%Ti (at.%). Inset of (b) shows a higher magnification BSE image of a grain boundary. The stress-strain curve of a bamboo structured tension sample of Fe-34.0%Mn-15.0%Al-7.5%Ni-1.5%Ti is shown in (c). The inset depicts an optical micrograph of two grains separated by an almost straight grain boundary after testing.