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Thermal cycling behavior of an aged FeNiCoAlTa single-crystal shape memory alloy

P. Krooß,[a] M.J. Holzweissig,[a,*] T. Niendorf,[a] C. Somsen,[b] M. Schaper,[a] Y.I. Chumlyakov[c] and H.J. Maier[d]

[a] *University of Paderborn, Lehrstuhl für Werkstoffkunde (Materials Science), 33095 Paderborn, Germany*
[b] *Ruhr-Universität Bochum, Institut für Werkstoffe, 44801 Bochum, Germany*
[c] *Tomsk State University, Siberian Physical Technical Institute, 634050 Tomsk, Russia*
[d] *Leibniz Universität Hannover, Institut für Werkstoffkunde (Materials Science), 30823 Garbsen, Germany*

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In this study the thermal cycling behavior of differently aged [1 0 0]-oriented Fe–28Ni–17Co–11.5Al–2.5Ta (at.%) shape memory single crystals was investigated. The strain–temperature response determined from thermal cycling experiments revealed a strong dependency on the precipitate morphology, which was adjusted by aging heat treatments. Specifically, a high precipitate density in the microstructure leads to small phase transformation-induced strains and low stresses necessary for activation of the martensitic phase transformation.

Keywords: Iron-based shape memory alloys; Microstructure; Precipitation hardening; Thermal cycling behavior; Clausius–Clapeyron

Fe-based shape memory alloys (SMAs) have recently attracted substantial research interest, due to their comparatively low material costs compared to conventional NiTi-based SMAs and the possibility of using steelmaking technology, reducing processing costs significantly [1–5]. Unfortunately, most of these alloys, such as FeMnSi, FeNiCoTi, FeNiC or FePt, cannot be employed for superelastic and damping applications due to their poor shape memory properties and/or the small recoverable transformation strains [6–8]. Recently, however, the Fe-based SMA FeNiCoAlTa was reported to feature superelastic transformation strains of up to 13% for a textured polycrystalline specimen and up to 6.8% superelastic strain for a single-crystal specimen [9–11]. For both the polycrystalline specimen as well as for the single-crystal specimen the highest superelastic transformation strains were obtained along the [1 0 0] loading direction. Most studies on FeNiCoAlTa SMA have focused on characterizing the transformation behavior following different aging heat treatments with the aim of maximizing the recoverable transformation strains [9–14]. For many applications, such as high-strength actuators, the cyclic stability is of paramount importance. However, a systematic analysis of the thermal cycling behavior of FeNiCoAlTa single crystals has not yet been reported. Thus, the current work was undertaken in order to determine the thermal cycling behavior of differently aged FeNiCoAlTa single-crystal SMA.

The material investigated was a Fe–28Ni–17Co–11.5Al–2.5Ta (at.%) alloy, which was initially produced by vacuum induction melting. Next, single crystals were grown from the ingot by utilizing the Bridgman technique in a helium atmosphere. After the heat treatment (solution annealing and aging) described below, the alloy exhibited shape memory properties. The crystal structure is face-centered cubic in the austenitic and body-centered tetragonal in the martensitic phase. For the experimental determination of the thermal cycling behavior, dogbone-shaped tensile specimens featuring a gauge section of 1.5 mm × 1.5 mm × 18 mm were electrodischarge machined such that the loading axis of the specimens was along the [1 0 0] orientation. In order to ensure a high surface quality the specimens were first

* Corresponding author. Tel.: +49 5251 60 5235; fax: +49 5251 60 3854; e-mail: martin.joachim.holzweissig@uni-paderborn.de

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mechanically ground down to a grid size of 5 μm and then electropolished using a perchloric acid solution. The solution heat treatment for all specimens was carried out at 1300 °C for 24 h in vacuum followed by water quenching, in order to ensure a homogenized microstructure. Subsequently, the homogenized specimens were subjected to different aging treatments, namely 48 h/600 °C, 72 h/600 °C, 90 h/600 °C, 0.5 h/700 °C and 1 h/700 °C, in order to create different $L1_2$ precipitate morphologies (γ'). These aging heat treatments produced substantially different precipitate volume fractions as well as sizes. For the thermal cycling experiments a nitrogen heating system was employed, which allowed for heating/cooling of the specimens in the range from −150 to 100 °C. During the thermal cycling experiments the specimens were loaded in a servohydraulic testing machine under force control. For a given stress level, the initial temperatures of the thermal cycle were chosen such as to be 30 °C above the austenite finish temperature (A_f) for the alloy after a specific heat treatment.

The thermal cycling behavior at various superimposed tensile stress levels for different aging heat treatments employed is illustrated in Figure 1, in which the transformation temperatures are exemplified by one hysteresis determined for a sample heat treated at 600 °C for 48 h. An immediate observation is that a reversible phase transformation was obtained for all heat treatments used, except for the one at 700 °C/0.5 h—apparently, this heat treatment was not sufficient to realize an appropriate volume fraction and/or size of the precipitates as well as providing a matrix composition that ensured an appropriate driving force for phase transformation. The precipitates both induce a coherency stress field and provide for a decomposed matrix, which are prerequisites for a reversible austenite-to-martensite phase transformation [1]. The reason for the missing phase transformation under the lower stress (750 MPa) is the low martensite start temperature (M_s) and M_f adjusted due to the heat treatment at 700 °C for 0.5 h as a consequence of the high content of solute elements within the microstructure. For the heat treatments showing a reversible phase transformation, an increasing (M_s) with an increasing superimposed stress level is obvious from Figure 1. The superimposed stress provides for an additional driving force such that the required Gibbs free energy for the phase transformation is reduced and hence the transformation is shifted to higher temperatures [1,10]. For the 700 °C/1 h heat treatment a reversible phase transformation can be observed in the tensile stress range from 500 up to 900 MPa, whereby at the latter stress level a residual strain of 0.5% results after a complete phase transformation cycle. The higher stress levels superimposed on the thermal cycles are possible because of the high yield strength of the matrix of the SMA and low density of crystal defects. In fact, Ma et al. [10] observed fracture of their FeNiCoAlTa shape memory single crystals during temperature cycling under 75 MPa superimposed stress. Ma et al. [10,12] aged their specimens, inter alia, at 600 °C for 90 h, and thus precipitates with an average size of 5 nm with a high volume fraction evolved. For the 700 °C/1 h aging treatment used in the present study, precipitates evolved which were larger in size (≈10 nm), cf. Figure 2. Apparently, the volume fraction of the precipitates is lower compared to those obtained with the heat treatment used by Ma et al. [10,12] as the hardness of the microstructure is significantly lower (Fig. 3a). As illustrated in Figure 1, both of the 600 °C heat treatments used yielded comparatively low stress levels superimposed on the thermal cycles, i.e. between 50 and 400 MPa for 48 h aging time and between 50 and 350 MPa for 72 h aging time. At higher stress levels the specimens fractured, i.e. at 500 MPa for the 48 h heat treatment duration and at 400 MPa for the 72 h/600 °C treatment. It is obvious that the stress superimposed on the thermal cycles decreases with increasing hardness (Figs. 1 and 2a). A similar phenomenon was observed by Krooß et al. [13], who found decreasing stress levels with longer heat treatment durations at a temperature of 700 °C. They traced the decreasing stresses back to an increasing precipitate size as well as a higher volume fraction. The higher magnitudes of inherent stress surrounding the precipitates reduce the external stress required for

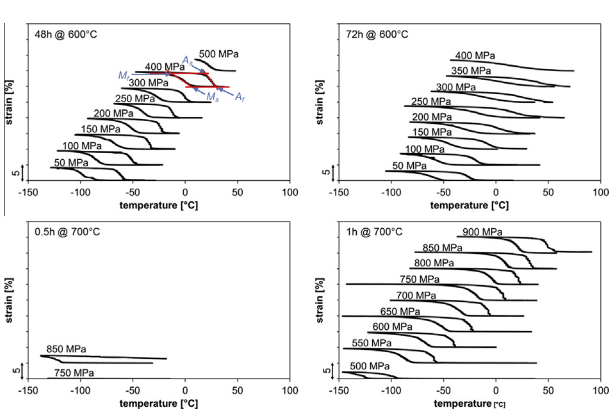

Figure 1. Strain–temperature response of the [1 0 0]-oriented FeNiCoAlTa single-crystal shape memory alloy during thermal cycling experiments with constant superimposed stress levels. See main text for details.

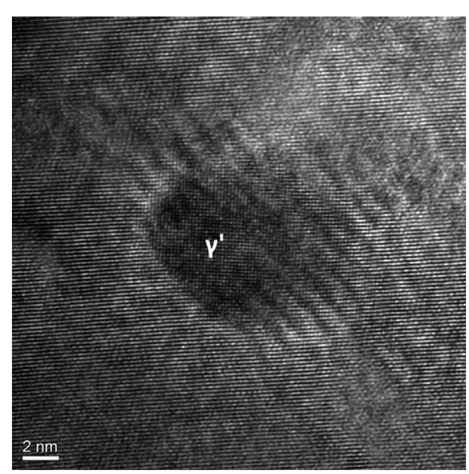

Figure 2. High-resolution transmission electron microscopy image illustrating a γ' precipitate in an [1 0 0]-oriented FeNiCoAlTa single-crystal shape memory alloy austenite matrix after a 700 °C/1 h aging heat treatment.

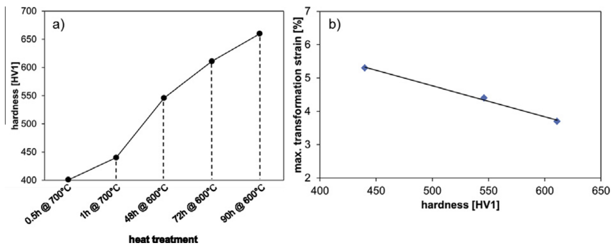

Figure 3. Hardness values resulting from the aging heat treatments (a) and the corresponding maximum transformation-induced strains (b) of the [1 0 0]-oriented FeNiCoAlTa SMA.

the onset of the phase transformation. This effect, in turn, appears to be one reason for the lower stress levels superimposed on the thermal cycles at higher hardness values of the FeNiCoAlTa alloy investigated in the present study.

In addition, the thermal hysteresis, i.e. the difference between A_f and M_s, is of great importance and is illustrated in Figure 1: a larger temperature hysteresis (max. 90 °C at 250 MPa) can be observed after the 600 °C/72 h heat treatment as compared to the temperature hysteresis observed after heat treatments at 600 °C for 48 h (max. 40 °C at 150 MPa) and at 700 °C for 1 h (max. 30 °C at 900 MPa). This effect is also attributed to the different precipitate morphologies resulting from the various aging heat treatments. In addition, the high hardness values indicate a high volume fraction of precipitates in the microstructure. Thus the probability of an interaction between the growing martensitic phase and the precipitates is high. This interaction, in turn, aggravates the martensitic growth, making additional supercooling of the austenitic phase necessary to attain the Gibbs free energy required for the completion of the phase transformation [1,10]. Furthermore, increasing hardness values indicate an increasing volume fraction of precipitates within the matrix and thus a decomposition of the matrix takes place, i.e. the fraction of the chemical elements which form precipitates is reduced in the matrix surrounding the precipitates. By reducing the fraction of the alloying elements in the matrix the driving force for the phase transformation derived from the chemical composition is affected, and thus it is necessary to balance the driving force for the phase transformation by supercooling the austenite [3,12–14].

In terms of the transformation strains, the specimen aged at 700 °C for 1 h exhibits the largest value with 5.2% under a superimposed stress of 900 MPa, whereas the specimens aged at 600 °C for 48 h (max. 4.6% at 200 MPa) and for 72 h (max. 3.7% at 150 MPa) exhibit lower transformation strains (Fig. 1). Figure 3b illustrates an increase in the maximum transformation strain with a decrease in hardness. The high transformation strains at low hardness values can again be attributed to the reduced interaction between the growing martensitic phase and the precipitates within the microstructure. Therefore, the growth of the martensite is less interrupted at low hardness values, providing for a more complete phase transformation and thus resulting in larger transformation strains [10,12].

Figure 4 summarizes the effect of the different heat treatments on the onset of the martensitic phase transformation in the [1 0 0]-oriented FeNiCoAlTa SMA single crystals. Again, a relationship between the precipitate morphology within the microstructure and the transformation behavior can be inferred, whereby a low precipitate volume fraction (700 °C for 1 h) needs higher stresses to initiate the martensitic transformation than a higher precipitate volume fraction (600 °C for 72 h). Furthermore, M_s increases with increasing superimposed stress level nearly linearly for all aging heat treatments investigated. This dependence of the stress (σ) necessary for initiating the martensitic transformation on the temperature (T) can be described by the Clausius–Clapeyron equation:

$$\frac{d\sigma}{dT} = -\frac{\Delta S}{V_m \varepsilon_{tr}},$$

where ΔS represents the transformation entropy, V_m is the molar volume and ε_{tr} represents the phase transformation-induced strain. For the cases considered in this paper the stress–temperature behavior depends only on the transformation strain since both ΔS as well as V_m are not affected by the direction of the stress applied and hence both variables can be considered as constants [10,15–18]. The slopes of the Clausius–Clapeyron plots are very similar for both aging treatments at 600 °C ($d\sigma/dT$ varies from 3.5 to 3.8 MPa K^{-1}), but the slope is slightly smaller for the heat treatment conducted at 700 °C ($d\sigma/dT = 2.8$ MPa K^{-1}). The results of this study are different to those determined by Ma et al. [12] who carried out their work on nominally the same type of single crystal. In particular, the slope in the Clausius–Clapeyron plot for the material heat treated at 600 °C/ 90 h was 4.12 MPa K^{-1}, i.e. slightly above the values determined in this study. Clearly, this alloy is very sensitive to small variations in chemical composition [18].

The current findings shed light on the thermal cycling behavior of [1 0 0]-oriented FeNiCoAlTa SMA single crystals. Specifically, an increase in the hardness of the microstructure results both in decreasing phase transformation-induced strains and a lower stress level needed for the onset of the martensitic transformation. This behavior can be attributed to (i) the interaction between the growing martensite plates and phase boundaries;

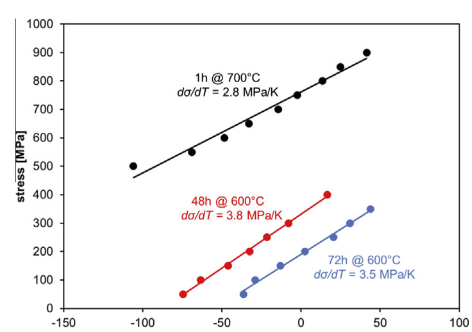

Figure 4. Required tensile stress for initiating the martensitic phase transformation of the [1 0 0]-oriented FeNiCoAlTa SMA for different aging heat treatments.

(ii) the coherency stress fields of the precipitates; and (iii) a change in the chemical composition of the matrix due to precipitation.

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