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# Impact of test temperature on functional degradation in Fe-Ni-Co-Al-Ta shape memory alloy single crystals

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ABSTRACT

The present paper focuses on the analysis of functional fatigue properties in ⟨001⟩-oriented single crystalline Fe-Ni-Co-Al-Ta shape memory alloys. Superelastic cycling experiments up to 4.5% at different temperatures were conducted and revealed excellent cyclic stability at lower testing temperatures. Transmission electron microscopy observations shed light on the influence of precipitation and dislocation activity on functional stability.

## 1. Introduction

Among Fe-based shape memory alloys (SMAs), Fe-Ni-Co-Al-Ta (FNCAT) SMA has attracted attention due to its low cost and good mechanical properties when compared with Ni-Ti [1,2]. FNCAT undergoes a martensitic transformation (MT) from $\gamma$ austenite (fcc) to $\alpha$' martensite (bct) [2,3]. The thermoelastic character of the MT in FNCAT is related to the presence of coherent, ordered $\gamma$' ($L1_2$) precipitates of $Ni_3Al$ type. Due to the formation of coherency stress fields, these fine precipitates strengthen the matrix of the parent phase [4–6]. However, the loss of functional properties, i.e. accumulation of residual strain and/or changes in the evolution of the stress strain hysteresis upon cyclic loading is one of the limiting factors towards industrial application. While for Ni-Ti based alloys numerous data detailing microstructural reasons for functional degradation were reported [7], cyclic properties of Fe-based alloys in the Fe-Ni-Co-Al-X (X = Ta, Nb, Ti) family are hardly available [6,8,9]. Microstructural mechanisms, which account for functional degradation of SMAs, can be rationalized by dislocation-induced pinning of phase boundaries, i.e. mechanical stabilization of martensite variants by local stress fields around dislocations. In turn, the lack of strength of either austenitic or martensitic phase allows for significant dislocation activity [6,10].

The current study focuses on the response of ⟨001⟩-oriented FNCAT single crystals to mechanical cycling. Fatigue tests in a temperature range between −130 °C and 20 °C and TEM analysis were performed in order to shed light on microstructural features governing functional instabilities.

## 2. Material and methods

Single crystals of Fe41-Ni28-Co17-Al11.5-Ta2.5 (at.%) were produced using vacuum induction melting and Bridgman technique under helium atmosphere. Dog-bone-shaped tensile samples with a gauge length of 8 mm and a cross section of 1.6*1.5 $mm^2$ were machined from bulk crystals with the ⟨001⟩ orientation parallel to the loading direction. A homogenization procedure was conducted in evacuated quartz glass tubes at 1300 °C for 24 h followed by water quenching. After homogenization samples were aged for 1 h at 700 °C under argon atmosphere to induce fine coherent $\gamma$ precipitates. Pseudoelastic cycling experiments up to 100 cycles were performed in displacement control using a servohydraulic test rig. A fixed maximum tensile strain of 4% upon loading and a minimum stress for unloading applying a displacement rate of 0.03 mm/s were set. Constant cooling was realized using a nitrogen

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heating/cooling system capable to operate at temperatures from -150°C to 100 °C. At −130 °C fatigue tests needed to be discontinued after 97 cycles due to the amount of nitrogen that was needed for cooling. Strains were measured using an extensometer with 12 mm gauge length directly attached to the samples. High-resolution transmission electron microscopy (HRTEM) analysis was conducted using a FEI Tecnai F20 operating at 200 kV. Sample preparation details for TEM can be found in previous work [6].

## 3. Results and discussions

Fig. 1 shows cyclic stress–strain responses obtained at −130 °C, −100 °C and 20 °C. At all test temperatures, an almost perfect pseudoelastic response is initially observed. However, significant irreversible strains accumulate during cycling at 20 °C leading to narrower stress-strain hysteresis in the final cycle, i.e. the material suffers functional degradation, since the available pseudoelastic strain is reduced upon cycling. This can be correlated to the accumulation of irreversible strain and the decrease of the stress level for the onset of the stress-induced martensitic transformation (SIMT). At −100 °C, changes in the cyclic evolution of the stress–strain hysteresis are also visible in the stress–strain diagram (Fig. 1). However, the accumulation of residual strain and the decrease of the critical stress level for SIMT ($\sigma_{crit}$) is less pronounced compared to the sample tested at 20 °C. Perfect cyclic stability without any kind of changes in the evolution of stress–strain hysteresis is found at −130 °C. Such excellent stability of the pseudoelastic stress–strain hysteresis during mechanical cycling in a Fe-based SMA is reported here for the first time. In addition, the evolution of $\sigma_{crit}$ versus temperature is shown for a temperature range from -150 °C to 20 °C (inset of Fig. 1). $\sigma_{crit}$ was taken from the first cycle in each condition. A slope of 2.5 MPa/°C is in good agreement with the Clausius-Clapeyron (CC) equation as previously shown for heating-cooling experiments [5].

In order to quantitatively measure cyclic degradation resistance, the evolution of $\sigma_{crit}$ and residual strain are plotted as a function of cycle number (Fig. 2). An almost linear increase of residual strain up to 1.4% in the final cycle is observed for the sample tested at 20 °C. The increase in residual strain correlates to a strong decrease of $\sigma_{crit}$, by ~ 70% at 20 °C. In contrary, both accumulated residual strain (<0.1%) and $\sigma_{crit}$ level, do not change upon cycling at −130 °C indicating the highest resistance against cyclic degradation. Even functional degradation at −100 °C seems to be hampered in correlation to the fatigue test at 20 °C, i.e. $\sigma_{crit}$ decreases relatively slow in each cycle and accumulation of residual strain is marginal (<0.2%). This already indicates a fundamental change in the functional degradation path when comparing 20 °C and −100 °C test temperature. The characteristic dislocation activity during cycling is thought to be responsible, as intensively discussed in [6]. Preliminary studies [4,10] have shown that the width of stress hysteresis ($\Delta\sigma$) can be an appropriate indicator for functional degradation of pseudoelastic properties upon cyclic loading. Once the elastic energy stored during the forward SIMT is dissipated by intense dislocation activity, i.e. plastic flow, the reverse transformation on stress relieving is hampered evoking an increased $\Delta\sigma$.

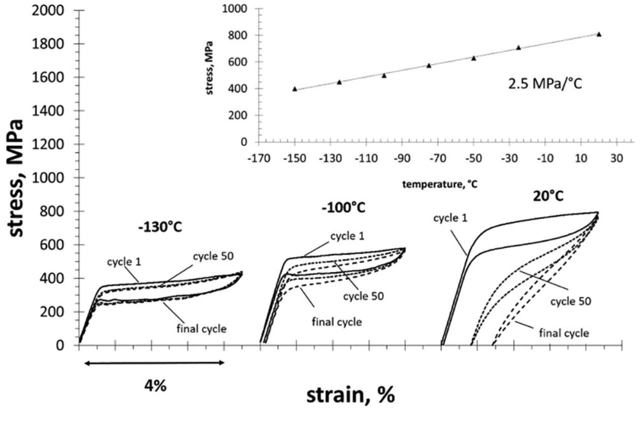

**Fig. 1.** Cyclic stress–strain responses at different test temperatures for ⟨001⟩-oriented FNCAT following aging at 700 °C for 1 h. The inset reveals the CC relationship. (partly recompiled from [6])

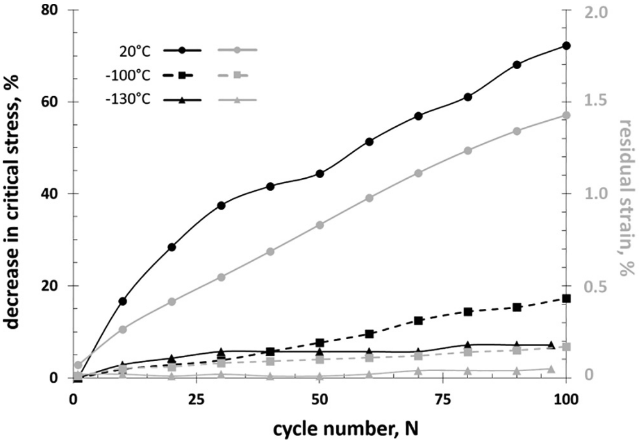

**Fig. 2.** Evolution of critical stress and residual strain vs number of pseudoelastic cycles. Data points were extracted from cycling experiments in Fig. 1.

As can be seen in Fig. 1 $\Delta\sigma$ of the initial cycle increases with test temperature, i.e. around 150 MPa at 20 °C, although the microstructure is similar for all the specimens in terms of crystallographic orientation and aging condition. Thus, an intense dislocation activity at elevated test temperatures is supposed to mechanically stabilize the martensitic phase during pseudoelastic cycling [4,5,6,11]. This assumption becomes more evident, when the CC relationship is correlated with the degree of functional degradation in each cycle. According to the steep CC relationship of 2.5 MPa/°C, $\sigma_{crit}$ becomes almost double as high at 20 °C as compared to −130 °C. Thus, the yield strength of the material may be exceeded leading to significant dislocation activity and therefore, to an increased $\Delta\sigma$. At −130 °C stresses are only around 400 MPa and, thus, are not expected to exceed the material strength. Consequently, the characteristic evolution of $\sigma_{crit}$ as well as the accumulated residual strain at each tested temperature are assumed to correlate to how far the yield strength is exceeded at a given test temperature.

In order to discuss the influence of precipitates on cyclic degradation behaviour, TEM analysis were performed on selected specimens (Fig. 3). The presence of the bct martensite is revealed in the vicinity of the $\gamma$ precipitates for all conditions, i.e. unloaded reference state (a-c), after cycling at RT (d-f) and after cycling at −130 °C (g-i). In addition, the austenite phase has been identified in all conditions as well, as can be seen on the diffraction pattern shown in Fig. 3. In all TEM micrographs the small precipitates are characterized by similar morphology and size, i.e. spheroidal shape with diameters up to 5–8 nm, in good correlation with values in literature [6,10,11]. Following fatigue testing at 20 °C, a distinct amount of mechanically stabilized martensite is found in the microstructure as was shown in the former study [6] supporting the aforementioned discussion. As expected, in the "non-fatigued" condition as well as following fatigue at −130 °C no cyclically pinned martensite is found nor is any significant dislocation activity present in the microstructure. In the previous work, Krooß

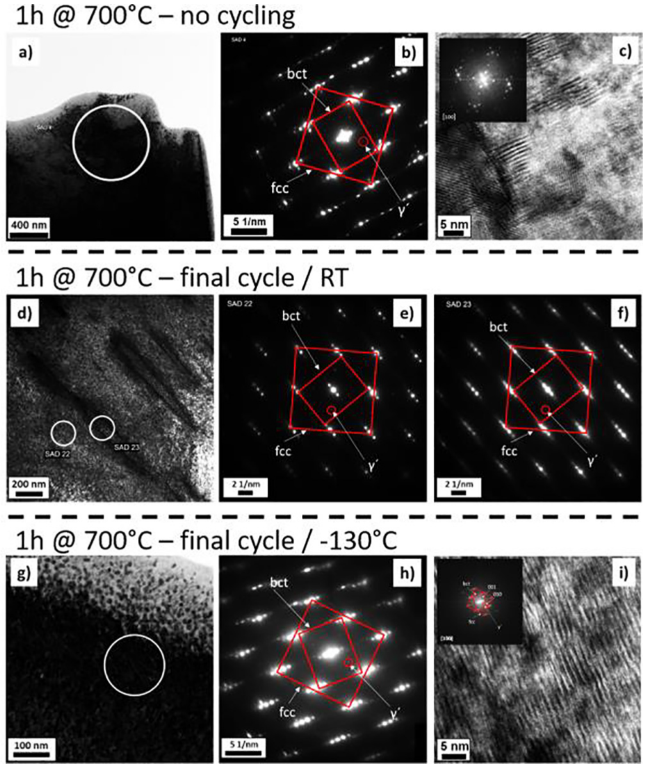

**Fig. 3.** TEM micrographs of ⟨001⟩-oriented FNCAT following aging at 700 °C for 1 h after different thermo-mechanical loading histories: Microstructure in the reference state without any cycling (a-c) and microstructural evolution after 100 cycles at RT (d-f) and 97 cycles at −130 °C (g-i). Fig. (a), (d) and (g) show TEM , while bright field images. Fig. (b), (e), (f) and (h) diffraction patterns from the encircled regions depicted in Fig. (a), (d) and (g), respectively. Please note, SAD 22 and 23 were obtained from the austenite matrix and a region consisting of austenite and cyclically stabilized martensite, respectively. Fig. (c) and (i) show high resolution TEM images together with FFT (Fast Fourier Transformation) as an inset in the upper left. All obtained in [001] zone direction.

et al. [6] suggested that the precipitates may have an impact on the fatigue properties, as they might be double sheared and, therefore, contribute to martensite stabilization and accelerated degradation. However, this study reveals that mechanical martensite stabilization does not occur during fatigue at low temperatures as can be deduced from the TEM analysis in the current work, indicating that double shearing of the precipitates may play a minor role with regard to the cyclic stability. It is most likely that the stresses during cycling at low temperatures are well below the yield strength of the material and, thus, no dislocation activity is present. It also seems to be likely that the stress fields generated by the precipitates seem to act as nucleation sites promoting the formation of martensite in its vicinity, however, the precipitates do not deteriorate the cyclic properties at low temperatures. Obviously, the former aspect can be deduced from the TEM analysis (Fig. 3a–c), since both, the austenite and martensite phase, could be identified in the vicinity of the particles, even without cyclic loading. Thus, the discussion in the previous chapter seems to be the most rational explanation for the rapid functional degradation under consideration of a given precipitate morphology. However, when the precipitate morphology changes with the heat treatment procedure conducted, the degradation mechanisms may also change accordingly. Preliminary studies have revealed the impact of different precipitate sizes on the functional thermo-mechanical response under monotonic loading in FNCAT SMAs [11]. Thus, the role of precipitate morphology, size and chemistry on the fatigue mechanisms will be part of follow-up studies.

## 4. Conclusions

The impact of test temperature on functional degradation in FNCAT was studied. For the first time in Fe-based SMA, excellent cyclic mechanical stability without any kind of changes in the evolution of the stress–strain hysteresis is observed in single-crystalline material tested at −130 °C. Rising test temperatures lead to an increasing intensity of irreversible processes, which result in a significant change in the evolution of the stress–strain response and, thus, deteriorate pseudoelastic performance upon mechanical cycling. Pronounced dislocation activity is seen to be the underlying microstructural mechanism for the accelerated accumulation of residual strains and the strong decrease of $\sigma_{crit}$ at elevated test temperatures, while precipitates of the present morphology seem to hardly influence the fatigue properties.

## CRediT authorship contribution statement

**Cesar Sobrero:** Investigation, Visualization, Writing - original draft. **Christian Lauhoff:** Conceptualization, Investigation, Writing - review & editing. **Dennis Langenkämper:** Investigation, Writing - review & editing. **Christoph Somsen:** Investigation, Writing - review & editing. **Gunther Eggeler:** Writing - review & editing. **Yuri I. Chumlyakov:** Conceptualization, Investigation, Writing - review & editing. **Thomas Niendorf:** Conceptualization, Writing - review & editing. **Philipp Krooß:** Conceptualization, Visualization, Project administration, Writing - review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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