Deformation behavior of multilayered NiFe with bimodal grain size distribution at room and elevated temperature

Jochen Fiebig^a, Jie Jian^b, Lilia Kurmanaeva^a, Jon McCrea^c, Haiyan Wang^b, Enrique Lavernia^{a,d},
Amiya Mukherjee^a

a -Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95817, USA

b- Department of Electrical and Computer Engineering, Texas A & M University, College Station, TX 77843-3128, USA

c- Integrin Technologies Inc., Toronto, Canada

d Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697

email-address corresponding author: jmfiebig@ucdavis.edu

Abstract

We describe a study of the temperature dependent deformation behavior of a multilayered NiFe-60wt%Fe alloy with a layer thickness of 5 μm fabricated by electrodeposition. The structure of adjacent layers alternates between a nanocrystalline and a coarse grained. Uniaxial tensile tests at temperature between 20°C and 400°C and strain rate of $10^{-4} - 10^{-2}$ were used to determine the mechanical behavior. Microstructure observations via transmission electron microscopy and fractography were performed to provide insight into the underlying deformation mechanism. The mechanical behavior is discussed in the context of the bimodal microstructure of multilayered samples and the contribution of each sub-layer to strength and ductility. The results reveal that even at higher temperatures the nanocrystalline layer determines the mechanical performance of multilayered materials.

Introduction

Multilayered (ML) materials are structures consisting of alternating layers, usually of different materials, that are designed to improve the properties compared to those of the individual components. An original study by Koehler [1] focused on improving the strength of ML materials and is based on the different line energies of the dislocations in the individual sub-layers. The mechanical properties of several systems (e.g. Cu/Ni [2,3,4], Cu/Nb [3, 4] or Cu/Cr [3, 4]) have been investigated to understand the deformation mechanisms in ML structures. The thickness of the individual layers was varied in these experimental studies [2, 3, 4] down to a few nanometers (e.g. 2 – 100 nm for Cu/Ni [2]), and an inverse Hall-Petch behavior, similar to that reported for nanocrystalline materials [5,6], was observed for Cu/Ni. Interestingly, all these works concluded that the influence of the interlayer interface on the mobility of dislocations is the key to understand the observed mechanical properties. To that effect, Misra and Wang published an overview of the influence of the layer thickness on the deformation mechanisms in ML structures [7]. In the range of layer thickness from tens of micron down to the submicron

($\approx 50\text{-}100\text{ nm}$ [7]) the strength of multilayered materials is controlled by dislocation pile-ups at the interlayer interphases similar to the Hall-Petch relationship [8, 9] in conventional polycrystalline materials. The strength of the ML structure increases proportional to the inverse square root of the layer thickness. As soon as the layer thickness decreases below approximately 100 nm the concept of the so-called confined layer slip has been proposed [10, 11]. In this case, a single dislocation loop moves parallel to the interface as demonstrated during in situ indentation of Cu/Nb with a layer thickness of 20 nm for Nb and 30 nm for Cu [12]. Yet, if the layer thickness decreases to a few nanometers (2-5 nm) experimental results indicated that the crossing of individual dislocations through the interlayer interface becomes the dominant deformation mechanism [13]. Further theoretical studies on this transition from multiple to single dislocation regime have been done by Misra et al. [14] and Fang and Friedman [15]. Misra et al. investigated a deformation map for ML materials with layer thickness and columnar grains size (grain boundaries are perpendicular to the interlayer interface) as variables to determine the dislocation activity. Depending on several parameters (Burgers vector, misfit of the adjacent layers and Poisson ratio of the softer layer) below a few nm of layer thickness and/or grain size, no dislocation pile-ups were formed [14]. A similar study was done by Fang and Friedman for polycrystalline ML materials [15]. Here also deformation maps depending on the layer thickness and grain size were determined.

Another important factor required to establish an understanding of the properties of ML structures involves the control of the interlayer interface structure. A study by Mara et al. presents the influence of the interface type on thermal stability of ML Cu/Nb with a layer thickness of 10 nm fabricated by accumulative roll bonding (ARB) [16]. In this material a highly ordered interface between Cu and Nb forms via deformation twinning and lead to high strength and exceptional thermal stability. A comparison of ML Cu/Nb with the same layer thickness of 20 nm but deformed by different ARB deformation routes (cross-rolled and longitudinally rolled) demonstrate the influence of the interface structure on the thermal stability [17]. The cross-rolled samples contained atomically flat Cu/Nb interfaces while the interface in the longitudinally rolled samples is faceted. These faceted interface stabilizes the material at high temperatures, which was validated by hardness measurements and obtaining the average layer thickness after certain heat treatments. Different combinations of pure elements in experiments and simulation, e.g. Cu/Nb [16, 17], Cu/Ni [18, 19] or Al/Ti [20, 21] with different lattice structures (fcc, bcc, hcp) were investigated with regard to the influence of the interlayer interface on properties as strengthening, thermal stability or phase stability.

In our research we selected the structure of the multilayered material to be different from that published in earlier studies. Instead of combining two different metals as in previous works, the studied ML material consists of alternating nanocrystalline (NC) and coarse grained (CG) layers of a NiFe alloy with similar composition. The NC layer strengthens the structure due to the grain boundary strengthening (Hall-Petch relationship) and the CG layer provides the ductility due to dislocation sources activity and the capability of dislocation multiplication and storage. In a related early study, Tellkamp et al. [60] explained the high strength and relatively good ductility

of cryomilled Al by the existence of a few large grains within the nanocrystalline microstructure (average grain size of 35 nm). A similar rationale was used by Wang and Ma [22] to explain the increase in strength in combination with good ductility of ultrafine grained Cu that was heat treated to generate a bimodal grain size distribution [22].

Instead of intermixing coarse and nanocrystalline grains the approach of the present study is to understand the mechanical behavior of a ML material consisting of NC and CG layers as it has been published by Kurmanaeva et al. [27] for a NiFe alloy and Daly et al. [61] for a ML NiCo alloy recently. Daly et al. reported that the yield and ultimate tensile strengths for the ML NiCo follow a rule of mixture relationship with respect to the tested monolithic NC and CG NiCo specimens. The tests were performed only at room temperature. In contrast to these results a rule of mixture was not observed by Kurmanaeva et al. [27] for ML NiFe, also tested at room temperature. Instead the measured yield and ultimate tensile strengths were higher than expected on the basis of the rule of mixture. Furthermore, the elongation to failure of the ML samples was less than that of the monolithic NC NiFe specimens [27]. Daly et al. reported a slightly enhanced ductility of the ML NiCo specimens compared with the NC NiCo [61].

Inspection of the published literature shows that most studies report mechanical behavior from testing performed at room temperature [2,3,4,27]. There are, however, some limited reports on tests at elevated temperature, such as a study of ML Cu/Nb by Mara et al. [23-26], for example. Our previous study on ML NiFe [27] compared the mechanical properties of ML NiFe alloy to those of monolithic CG and NC NiFe samples. The tests were only completed at room temperature and at one selected strain rate. In the present study we focused on the mechanical behavior dependence on strain rate and testing temperature in order to provide insight into the dominant deformation mechanisms. Fractographic and microstructure analysis was completed using secondary electron microscopy (SEM) and transmission electron microscopy (TEM), respectively, on samples studied after tests at different test temperatures.

Experimental Methods

The multilayered Ni-60 wt.-%Fe samples were fabricated via pulsed electrodeposition by Integran Technologies Inc. in Toronto, Canada (details can be found in [67]). The modulated microstructure with alternating coarse and nanocrystalline layers was achieved by changing the electrodeposition parameters, namely voltage, current and pulse length. The layer thickness in the present study is 5 μm with a thickness ratio of 1:1. Thus, large sized sheets with a total thickness of 600 μm were produced by depositing on a passivated Titanium cathode. Afterwards the deposited material was mechanically stripped to obtain free-standing sheets from which the tensile specimens were sectioned by using EDM. The material contains a slight amount of impurities (Chemical composition C: 0.026 %, S: 0.018 %, N: 0.0004%, Co: 0.06 %, Cu: 0.014 % and Mo: 0.017 %, all in wt.-% [27]).

Uniaxial tensile tests were performed with a mini-tensile tester with a displacement resolution of 5 μm and a load resolution of 0.01 N controlled by LabVIEW software. The test temperature was selected between room temperature (RT, $0.17 \cdot T_m$) and 400°C ($0.4 \cdot T_m$) at strain rates between 10^{-4} s^{-1} and 10^{-2} s^{-1} . The gauge section of the dogbone-shaped tensile specimens measured 3 mm x 1 mm x 0.3 mm. All surfaces were mechanically polished to a mirror-like quality. Prior to each high temperature tensile test the chamber was first evacuated for several hours and the samples were heated to 100°C for 4h to get rid of any moisture inside the chamber. The tests itself were obtained under a positive (1 Psi pressure) high purity argon atmosphere (99.999% Ar). Argon was used as a protective gas to avoid oxidation of the specimens during the tensile tests. The strain rate sensitivity was calculated by:

$$m = \frac{\partial \ln \sigma_{YS}}{\partial \ln \dot{\epsilon}} \quad (1)$$

here m is the strain rate sensitivity, $\dot{\epsilon}$ is the strain rate and σ_{YS} is the yield stress. The activation volume can be obtained by:

$$\Delta V = \sqrt{3} k_B T \frac{\partial \ln \dot{\epsilon}}{\partial \ln \sigma_{YS}} \quad (2)$$

here k_B is the Boltzmann constant, T is the absolute temperature, $\dot{\epsilon}$ is the strain rate and σ_{YS} is the yield stress.

The thermal stability was investigated by using a differential scanning calorimeter (DSC) 404F3 by Netzsch. DSC measurements were performed at two different heating rates 20 and 30 K/min under a protective argon atmosphere. The sample weight was between 60 and 90 mg. The furnace of the DSC was purged for 10 min prior to each measurement. The peak temperatures were determined with the Proteus Analysis software provided by Netzsch.

A JEOL JEM-2010 microscope was used to perform the cross-sectional TEM (XTEM) and selected-area electron diffraction (SAED). The work was done under 200KV with a double-tilt holder and a point-to-point resolution of 0.23 nm. Conventional TEM sample preparation routine including cutting, gluing, grinding, polishing, and final precision ion polishing was used to prepare the XTEM foils.

The fracture surfaces were studied using scanning electron microscopy FEI 30 SEM at 5 keV.

Experimental results:

The stress-strain curves of ML NiFe samples at different strain rates at 20°C (room temperature, $0.17 \cdot T_m$) and 400°C ($0.4 \cdot T_m$) are plotted, in Fig. 1a) and 1b) respectively. At RT the ultimate tensile stress (UTS) is in the range of 1300-1500 MPa and decreases to 800 MPa at 400°C . These results show that the UTS at room temperature is not sensitive to the strain rate, so the stress levels are comparable for all strain rates. At 400°C however, both the yield stress (YS) and

the UTS are sensitive function of the strain rate. As expected the UTS decreases with increasing temperature, see Fig.1c). With increasing of testing temperature the strain rate sensitivity increases and activation volume decreases as it can be seen in Fig. 1d). The values of the strain rate sensitivity and activation volume are between 0.03-0.1 and 15 to 25 b^3 depending on temperature, respectively. The uniform elongation of the ML NiFe samples increases from 4.9% [27] at room temperature to around 12% at 400°C for a strain rate of 10^{-4} .

Fig. 2 a) – d) represent the fracture surface of NiFe with 5 μm layer thickness after a tensile test at room temperature (Fig. 2a) and b)) and at 400°C (Fig. 2c) and d)). At RT the NC layer is covered with small dimples that have the size of a few grains [28, 29]. Similar dimples were observed on the fracture surface of NC NiFe in our previous study [27]. It can be seen from Fig.2a) and 2b) that the layer thickness of the CG layer after the tensile test is smaller than 5 μm , as a result of plastic deformation. At elevated temperature (Fig.2c-e) the material partly is pulled out (see fig. 2e, circle indicates the regions) of the surface and the dimple size increases significantly from 50-100 nm at 20°C to 300 to 500 nm at 400 °C.

In our previous work on ML NiFe we found that the average grain size in the as-prepared state in the CG layer is about 500 nm and about 16 nm in the NC layer [27]. The grains in the coarse grained layer are elongated along the growth direction of the electrodeposition, which is perpendicular to the interface. Figures 3 represents bright field (Fig. 3a, 3b) and dark field TEM (Fig. 3c,3d) images of the microstructure after a tensile test performed at RT at a strain rate of 10^{-4}s^{-1} . In the CG layer there are no obvious microstructure changes observable, the layer thickness close to the fracture surface decreased approximately by 20%, from 5 μm down to 4 μm (fig. 3b).

Interestingly, the tensile test at RT led to the formation of in-between layers with finer grains (formed in between the CG layer and the NC layer), which elongated along the tensile direction and parallel to the interface. Some of these finer grains contain twins. We will refer to these layers as “fine layers” through the rest of the manuscript. The thickness of the one fine layer is less than 0.5 μm . These fine layers were not observed in the as-prepared state.

Figure 4a presents SEM cross-section image taken close to the fracture surface of ML samples tested at 400°C at a strain rate of 10^{-4}s^{-1} . Testing at elevated temperatures resulted in the formation of densely located pores elongated in tensile direction, see fig. 4b. The observed pores in the TEM image can be a result of the sample preparation process. But since pores were also observed in the SEM image (fig. 4a) it is likely that the pores observed in TEM image are not due to preparation artefacts. The microstructure of the NC layer after a tensile test at 400°C at a strain rate of 10^{-4}s^{-1} is still equiaxed, but the average grain size increased up to 100-150 nm (Fig. 4c). In addition a few larger grains can be observed in the vicinity of the nanograins, as it can be seen from fig. 4d). From the SAD pattern of the nano grained (fig. 4e) and large grained areas (fig. 4f) it can be seen that after a test at 400°C fcc and bcc NiFe are present, as it was observed in the as-prepared state in our previous work [27].

Fig.5 shows our calorimetric measurements. Two different heating rates, 20 K/min (fig. 5a) and 30 K/min (fig. 5b), were used. The determined peak temperatures are indicated by dotted lines. For each measurement two runs were performed. The second run was used to determine the nature of the observed process, reversible or irreversible. The exothermic peaks of the irreversible reactions are observed at 406.2 °C and 420.3 °C, respectively.

Discussion

Deformation mechanism in ML NiFe at room temperature

At low temperature the fracture surface of the NC layer is covered with small dimples with an average size of 50 to 100 nm (see Fig. 2b). This “cup-cup” structure is typical for NC materials and occurs due to the formation of nanocracks and their transformation into pores. These pores grow and form local necks between them [29]. An alternative origin for the dimple formation is intragranular slip coupled with unaccommodated grain boundary sliding resulting in void formation at the grain boundaries [30] (close to the fracture surface voids were observed, see figure 4). These voids can grow and form the observed dimple structure as described in more detail by Kumar et al. [28]. Daly et al. [61] observed a sequence of coarse and fine dimpled structure on the fracture surface of ML NiCo which correspond to microvoid coalescence in the CG and NC layers respectively. Due to the different flow properties of the NC and CG layer, the simultaneous deformation of the ML sample leads to fracture of the hard phase and following to necking and fracture of the soft phase as observed for Cu/Cr ML [31].

At room temperature ($0.17 \cdot T_m$) we could not observe an increase of the yield stress (or ultimate tensile stress) with increasing strain rate which indicates that the strain rate sensitivity is small. The interpretation of this value has to take into account the properties of each layer since due to the different average grain sizes different deformation mechanisms could be active. To understand the influence of the different layers on the overall deformation behavior we first look at possible deformation mechanisms in the CG and NC layer separately, starting with results measured at RT.

According to our previous SEM study the grains in the CG layer are columnar with a width of 500 nm [27]. In this grain size regime the deformation behavior is controlled by dislocation movement and multiplication. As mentioned in our previous study the grains in the CG layer of the electrodeposited NiFe grow preferably with a (100) orientation along the electrodeposition direction [27], perpendicular to the tensile direction. During the tensile deformation the dislocations glide along the (110) directions on the (111) slip planes. These dislocations pile-up at grain boundaries and the NC/CG interlayer interfaces. At the interlayer interface the initiation of plastic deformation, dislocation movement, in the NC phase is unlikely since the capability for dislocation storage in nanograins is very limited. These pile-ups create a back stress that can affect the movement of dislocations moving on the same glide plane [27] which leads to work hardening of the CG layer. Experimental results show that the strain rate

sensitivity at room temperature in the coarse grained regime for fcc materials is below 0.01 [32-35], which refers to the fact that the rate controlling deformation mechanism is the thermally activated passage of dislocations overcoming localized obstacles.

In bulk NC Ni and Ni alloys the strain rate sensitivity at RT was found to be between 0.01 and 0.03 depending on the used testing method [34,36-40]. For an electrodeposited NC Ni-50%Fe alloy, also produced by Integran, Van Swygenhoven et al. found a significantly lower strain rate sensitivity of $m = 0.006$ at room temperature [41]. In their work the strain rate sensitivity was investigated for a wider strain rate interval (between $6 \cdot 10^{-7} \text{s}^{-1}$ and $3 \cdot 10^{-2} \text{s}^{-1}$). For the present study a comparable strain rate sensitivity would result in a difference of 2.8% (approximately 40 MPa, is within the error of the measurement of the sample thickness, $0.3 \text{ mm} \pm 0.01 \text{ mm}$ equals 3.3%) for the yield stress (ultimate stress) at $1 \cdot 10^{-4} \text{s}^{-1}$ and $1 \cdot 10^{-2} \text{s}^{-1}$. A similar value of 0.0052 was reported by Fan et al. for a Ni-18%Fe alloy with an average grain size of 23 nm [42]. As possible reasons Fan et al. proposed a reduced grain boundary mobility due to the presence of solutes and stress-induced grain growth [42]. Van Swygenhoven et al. explained their observation by a reduced dislocation mobility caused by local variations in chemical composition and/or a reduced lattice friction due to the presence of solutes [41].

Another factor which influences the strain rate sensitivity, in particular in the investigated material, could be the presence of bcc NiFe as shown by XRD analysis in our previous study [27]. Earlier research on electrodeposited of NiFe alloys have revealed a coexistence of bcc and fcc around a composition of 60 wt.-% Fe [43]. The presence of a second phase leads to the formation of bcc/fcc interfaces which can hinder the movement of dislocations in a different way than fcc/fcc interfaces since the coherency is lost and the Burger vectors in fcc and bcc phase are different from each other. Exceptions are special relationships between fcc and bcc like the Kurdjumov Sachs relationship [63].

In related studies Wei et al. compared the influence of the grain size on the mechanical properties of fcc and bcc materials [44]. It was found that the strain rate sensitivity of NC bcc is reduced in comparison to CG bcc materials. For instance the strain rate sensitivity for bcc Fe with an average grain size of 20 nm is 0.006 [44]. This behavior is contradictory to observations for fcc materials in the literature. This can be understood by looking at the different deformation mechanisms in fcc and bcc materials. In [44] the strain rate sensitivity is given by:

$$m = \frac{k_B T}{\tau \cdot v} = \frac{k_B T}{\tau \cdot l \cdot b \cdot \xi} \quad (3)$$

here k_B is the Boltzmann constant, T is the absolute temperature, τ is the applied stress, v is the activation volume, l the length of the dislocation segment involved in the thermally activated step, b is the Burgers vector and ξ is the length of the step.

In fcc materials forest dislocations are the principal obstacles for mobile dislocations. The applied stress depends on the dislocation density and the grain size. According to [44] the

Friedel sampling length has two different limits. For small grain sizes, the Friedel sampling length is proportional to the grain size ($l_2 \propto d$) and for large grain sizes or high dislocation densities the Friedel sampling length is inverse proportional to the square root of the forest dislocation density ($l_1 \propto 1/\sqrt{\rho}$) [44]. By using this different limits Wei et al. showed that for small grain sizes the strain rate sensitivity in fcc materials increases with decreasing grain size [44].

For bcc metals the deformation at low temperatures is controlled by the kink pair nucleation mechanism. This process is the rate limiting step for a wide range of grain sizes. As a result Wei et al. pointed out that the activation volume would decrease with applied stress and level off [44]. The strain rate sensitivity is proportional to the inverse of the applied stress. With decreasing grain size the applied stress increases and that causes the decrease in strain rate sensitivity [44].

But as discussed later also grain boundary mediated deformation processes, e.g. grain rotation, could contribute to the deformation behavior at room temperature, in particular in the NC layer. For grain boundary activity you would expect a value for m of 0.3 to 0.5 as it was observed for ML Cu/Nb at high temperature [23].

In summary there are several factors that could reduce the measured strain rate sensitivity which are the presence of fcc and bcc NiFe which could influence the dislocation mobility, a reduced dislocation mobility due to variations in chemical composition or reduced lattice as mentioned by Van Swygenhoven et al. [41] or as suggested by Fan et al. a reduced grain boundary mobility and stress induced grain growth [42].

Deformation mechanisms at elevated temperature

Prior to the mechanical properties at elevated temperature we would like to discuss the thermal stability of the ML NiFe specimens. Previously Liu et al. [66] studied the thermal stability of an electrodeposited NiFe alloy (37 weight-% Ni). Where the alloy contains only the fcc NiFe phase. Liu et al. detected the exothermic peaks in the temperature range of 373-410°C, which is in good agreement with our results. Additionally the activation enthalpy was calculated to be around 120 kJ/mol [66].

Based on our results and earlier work of Liu et al. [66] we assume that although grain growth starts at 400°C, during the tensile tests microstructure is in a steady state condition. According to [66] study the NC NiFe alloy does not grow in the first two hours at 350°C (623 K). At a temperature of 400°C (673 K) the grains growth is not significant, during the first two hours the average grain size increases from 12 nm to 30 nm [66], the fastest grain growth takes place in the first 1800s (30 min) and afterwards the grain size stabilizes. In our experiments (see experimental details) the heating of the samples to testing temperature takes around 40 min. Following the grain should be in a steady state condition during the test.

With increasing of testing temperature the material softens significantly and starting from 300°C the strain rate sensitivity becomes measurable (Fig. 1b,c). According to studies obtained by Martinez-Blanco et al. [45] (mechanically alloyed Fe₇₀Ni₃₀ and Fe₇₅Ni₂₅ with a grain size around 20 nm) and Nakayama et al. [46] (NiFe alloys with 25 to 58 wt.-% Fe, grain size of) the bcc NiFe phase transforms back into fcc NiFe when the temperature exceeds 300°C or 350°C, respectively. These two studies indicate that in the NiFe alloy the fraction of bcc partly or fully transforms back into fcc NiFe above 300 °C. In terms of crystal structure variation the investigated NiFe alloy might becomes more homogeneous at elevated temperatures since the amount of bcc/fcc interfaces decreases and dislocations have an easier time crossing the interface. The influence of thermal treatments on the microstructure is part of ongoing research. However, we should note here, that based on preliminary results, after testing at 400 °C the bcc phase still could be detected using electron diffraction.

The calculated activation volume of 15 b³ (400°C = 0.4 T_m) and 25 b³ (300°C) indicates that the NC layer still dominates the plastic behavior of the ML NiFe alloy at elevated temperature. The activation volume can be written as:

$$v = b \cdot l \cdot \xi = l \cdot b^2 \quad (4)$$

Here b, l and ξ have the same meaning as in equation 3. Therefore, the length of the moving dislocation segment is between 15 and 25 b at elevated temperature. For fcc materials the Friedel length can be understood as the distance between obstacles and the dislocations bow in between of them. If only forest dislocations are considered as obstacles for the dislocation glide this would lead to a dislocation density of approximately $2.5 - 6.9 \cdot 10^{16} \text{ m}^{-2}$. Van Swygenhoven et al. reported a relatively high dislocation density of $2.6 \cdot 10^{16} \text{ m}^{-2}$ for the investigated nanocrystalline Ni₅₀Fe₅₀ alloy (average grain size of 10 to 13 nm) produced via electrodeposition [47]. The estimated dislocation density based on the activation volume of the tested NiFe alloy in the present work is in reasonable agreement with the measured dislocation density in electrodeposited NiFe by Van Swygenhoven et al. [47]. It is important to note, however, that they measured this dislocation density by X-Ray diffraction (XRD). Furthermore dislocations should annihilate at elevated temperature and following the dislocation density decreases. An alternative to rationalize the low activation volume in ML NiFe involves a model by Cheng et al. [48] that treats the grain boundaries as Frank-Read like sources (Frank-Read like since the dislocations only can bow out of the boundary but not form a closed loop). In this case the critical sources length in their model is [48]:

$$L = c \cdot d \quad (5)$$

Here c is a numerical constant smaller than 1 (Cheng et al. analyzed the cases of c= 0.05, 0.1 and c=0.2 [48]) and d is the grain size. This model is appropriate for NC materials since here the grain size is so small that normal Frank-Read sources maybe cannot be activated due to the high stresses required. For c = 0.2-0.4 and a grain size of 16 nm, for simplicity the average grain size of the NC layer from our previous work was used [27] and it was assumed that there is no

grain growth, the source length is between 3.2 to 6.4 nm which is approximately 12-24b. The prediction of the model is in reasonable agreement with our experimental results. This indicates that between 300°C and 400 °C the deformation behavior of the ML NiFe alloy is still dominated by the properties of the NC layer.

With increasing temperature the strain rate sensitivity slightly increases up to 0.1 but these values are still below the theoretically predicted strain rate sensitivity for grain boundary sliding ($m = 0.5$ [49]) or coble creep ($m=1$ [50]). Mara et al. measured values for the strain rate sensitivity between 0.35 and 0.8 for ML Cu/Nb specimens at high temperatures and low strain rate (600 - 700°C, $1.0 \cdot 10^{-4} \text{ s}^{-1}$) and concluded that grain boundary sliding is a possible deformation mechanism [23]. Due to the increased temperature diffusion mediated deformation mechanisms, e.g. grain rotation and grain boundary sliding are more likely to occur. Using the grain boundary diffusion data obtained by Divinski et al. we can calculate that the grain boundary diffusion increases between 20 and 400°C by orders of magnitude (at 20°C: $2.38 \cdot 10^{-32} \text{ m}^2 \text{ s}^{-1}$ 400°C: $1.71 \cdot 10^{-16} \text{ m}^2 \text{ s}^{-1}$) [51]. A grain rotation model by Harris et al. [64], which uses the energy gradients with respect to misorientation as driving force, leads to a linear dependence of the rotation rate to the grain boundary diffusion coefficient. Furthermore the rotation rate is proportional to d^{-4} . According to this model grain rotation is favorable in small grains and elevated temperature, as long as the grain size does not increase. It is likely that in this temperature range more than one deformation process is active and the sample deforms partly by dislocation activity and partly by grain boundary mediated plasticity. These collective mechanisms could explain the pulled out material observed on the fracture surface above a temperature of 300°C.

As pointed out by Ivanisenko et al. [62] the application of kinetic analysis alone, determination of strain rate sensitivity and activation volume, might not be sufficient to understand the deformation mechanisms in the present work. To fully understand the presented results further work, in particular microstructure analysis or in-situ tests, are necessary.

Influence of the deformation on the microstructure at room temperature

As it can be seen from the TEM images several “fine grained layers” formed in between the CG and NC layer during the tensile test at RT (Fig. 2). The origin seems to be the interlayer interphase between the NC and CG layer, since we observed sometimes only two or three fine layers (these layers were observed next to the interlayer interface) and sometimes the entire NC layer consists of fine layers. In the following we propose a mechanism for the formation of these fine grained layers (also see Fig 6.). As already stated earlier the average grain size in the nanocrystalline layer is significantly smaller than that in the coarse grained layer. Thus, at the interface one grain in the coarse grained layer has several grains in the nanocrystalline layer as its neighbors, which might result in a small orientation difference between these nanograins. As observed during the in situ room temperature deformation of NC Ni [52,53], a few of these grains may rotate against each other and coalesce into one larger grain. A small orientation difference would favor this deformation mechanism. Wang et al. [53] present a model to

describe the grain rotation based on gliding grain boundary dislocations. This proposed grain rotation will be assisted by the presence of internal stresses at the interlayer interface caused by dislocation pile-ups at the interlayer interface. During further deformation these newly formed fine grains grow along the tensile direction due to stress assisted grain boundary motion. Stress assisted grain boundary motion has been observed close to the crack tip during in situ TEM studies in NC Aluminum thin films [65].

An alternative explanation for the formation of the fine layers is based on the different onset of the plastic deformation in the NC and the CG layer. The grains in the CG layer plastically deform earlier than the grains in the NC layer (Yield stress of the monolithic CG specimens is 320 MPa compared to 1357 MPa for the NC specimens, measured by tensile tests [27]). In the CG layer several dislocation sources are active. This dislocation activity in the CG layer leads to dislocation pile-ups at the interlayer interface and following to stress fields at the interface. In the NC grains close the CG/NC interface are now stresses in tensile direction and stresses caused by the dislocation pile-ups in the CG layer. This change in the stress-strain fields at the interface might results in an accelerated stress-assisted growth of NC grains close to the interface.

Within the “fine layers” multiple twins were observed. A simple explanation of the influence of grain size on the nucleation of deformation twins was given by Chen et al. [54]. They compared the critical stress needed to nucleate a perfect dislocation with the stress necessary to initiate a Shockley partial dislocation to generate stacking faults and deformation twins. For the perfect dislocation the source size was assumed to be equal to the grain size. This leads to the following equation for a critical grain size. Below this grain size the deformation is dominated by partial dislocations which should lead to the formation of deformation twins [54].

$$D_c = \frac{2G(b_N - b_p)b_p}{\gamma} \quad (6)$$

Here G is the shear modulus (54 to 58 GPa for NiFe [55]), b_N is the Burgers vector of a perfect dislocation, b_p is the Burgers vector of a Shockley partial and γ is the stacking fault energy. The stacking fault energy for NiFe, as a function of composition depending was investigated by Raymond et al. using X-Ray diffraction line profile analysis. From this study, for a Ni content of 40-wt.% γ is about 0.1 J/m² [56]. For a normal fcc structure the Burgers vector of a perfect dislocation is $a/2 \langle 110 \rangle$ (with lattice constant of $a = 0.358\text{-}0.359$ nm [57]) and for a Shockley partial dislocation $1/6 a \langle 112 \rangle$. For the investigated NiFe alloy this equation gives a grain size of approximately 15-25 nm. Partial dislocations would be favored, according to his simple model, in the nanograins.

In the case of bcc NiFe Niles and Owens [58] obtained an onset stress of around 360 MPa for twinning at low temperatures. Their alloy contained 25-wt.% of Ni. A general observation for bcc metals and alloys is that the onset stress for twinning seems to be temperature independent as pointed out by Meyers et al. [59]. For fcc metals it has been observed that the

twinning stress (for instance in Cu and Cu-alloys) is proportional to the square root of the stacking fault energy divided by $G \cdot b$. Based on this arguments alone it is not possible to predict which lattice structure is more likely to form twins during the deformation process. This is part of an ongoing investigation and requires an in depth study of the twinned grains.

Conclusions

The mechanical properties of a multilayered NiFe alloy with 5 μm layer thickness with modulated grain size have been investigated. At low temperatures the measured strain rate sensitivity of the ML material could not be estimated in the selected strain rate interval which could be explained by several factors, e.g. the coexistence of fcc and bcc NiFe. The stress induced by dislocation pile-ups at the interlayer interface leads to the formation of fine grained layers by grain rotation and grain coalescence at low temperatures. At elevated temperature the measured activation volume indicates that the bowing of dislocation from grain boundaries in the nanocrystalline is the dominant deformation mechanism while at even higher temperature grain boundary mediated deformation mechanisms might contribute to the overall deformation behavior.

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References:

- [1] J.S. Koehler *"Attempt to Design a Strong Solid"*, Phys. Rev. B, Vol.2 (2) (1970), 547-551
- [2] M. Verdier, M. Niewczas, J.D. Embury, M. Hawley, M. Nastasi and K. Kung, *"Plastic behavior of Cu/Ni multilayers"*, Mat. Res. Soc. Symp. Proc. 522 (1998), 77-82
- [3] H. King, A.M., M. Nastasi, T. Mitchell, M. Hawley, S. Swaminarayan, M. Verdier, M. Hundley, R. Hoagland, D. Embury and J. Hirth, Art Voter, *"Optimum design of ultra-strength nanolayered composites"*, Report, Los Alamos National Laboratory
- [4] A. Misra, J.P. Hirth and H. Kung, *"Single-dislocation-based strengthening mechanisms in nanoscale metallic multilayers"*, Scripta Mater., 82(16) (2002), 2935-2951
- [5] A.H. Chokshi, A. Rosen, J. Karch and H. Gleiter, *"On the validity of the Hall-Petch relationship in nanocrystalline materials"*, Scripta Metall. 23 (10) (1989), 1679-1683

- [6] J. Schiotz, F.D. Di Tolla and K.W. Jacobsen, "*Softening of nanocrystalline metals at very small grain sizes*", Nature 391 (1998), 561-563
- [7] J. Wang, A. Misra, "*An overview of interface-dominated deformation mechanisms in metallic multilayers*". Solid State and Materials Science 15 (2011), 20-28
- [8] E.O. Hall, Proc. Phys. Soc. London, B64, 747 (1951).
- [9] N.J. Petch, J. Iron Steel Inst. 174, 25 (1953).
- [10] Embury, J.D. and J.P. Hirth, "*On dislocation storage and the mechanical response of fine-scale microstructures*". Acta Metall. et Mater., 1994. 42(6), 2051-2056.
- [11] Srolovitz, D.J., S.M. Yalisove, and J.C. Bilello, "*Design of Multiscalar Metallic Multilayer Composites for High-Strength, High Toughness, and Low Cte Mismatch*". Metallurgical and Materials Transactions a-Physical Metallurgy and Materials Science, 1995. 26(7), 1805-1813
- [12] N. Li, J. Wang, A. Misra and J.Y. Hunag, "*Direct observation of confined layer slip in Cu/Nb multilayers*", Microsc. Microanal. 18 (2012), 1155-1162
- [13] A. Misra, J. P. Hirth and H. Kung, "*Single-dislocation-based strengthening mechanisms in nanoscale metallic multilayers*", Phil. Mag. A 82(16) (2002), 2935-2951
- [14] A. Misra, M. Verdier, H. Kung, J. D. Embury, and J. P. Hirth "*Deformation mechanism maps for polycrystalline metallic multilayers*", Scripta Materialia 41 (9) (1999), 973–979
- [15] L. Fang and L.H. Friedman, "*Analytic treatment of metallic multilayer strength at all length scales: Influence of dislocation sources*", Acta Materialia 55 (2007) 1505–1514
- [16] S. Zheng, I.J. Beyerlein, J.S. Carpenter, K. Kang, J. Wang, W. Han and N.A. Mara, "*High-strength and thermally stable bulk nanolayered composites due to twin-induced interfaces*", Nature communications, 4 (2013) DOI: 10.1038
- [17] S. Zheng, J.S. Carpenter, J. McCabe, I.J. Beyerlein and N.A. Mara "*Engineering interface structures and thermal stabilities via SPD processing in bulk nanostructured materials*", Scientific reports 4 (2014), DOI: 10.1038
- [18] K.O. Schweitz, J. Chevallier, J. Bøttiger, W. Matz and N. Schell, "*Hardness in Ag/Ni, Au/Ni and Cu/Ni multilayers*", Phil. Mag. A 81 (2001), 2021-2032
- [19] R.G. Hoagland, T.E. Mitchell, J.P. Hirth and H. Kung, "*On the strengthening effects of interfaces in multilayer fee metallic composite*", Phil. Mag. A 82 (2002) p.643.
- [20] R. Banerjee, X.-D. Zhang, S.A. Dregia and H.L. Fraser, "*Phase stability in Al/Ti multilayers*", Acta mater. 47(4) (1999), 1153-1161
- [21] R. Banerjee, S.A. Dregia and H.L. Fraser, "*Stability of fcc Titanium/Aluminum multilayers*", Acta mater. 47(15) (1999), 4225-4231
- [22] Y.M. Wang and E. Ma, "*Three strategies to achieve uniform tensile deformation in a nanostructured metal*", Acta Mater. 52(6) (2004), 1699-1709
- [23] N.A. Mara, T. Tamayo, A.V. Sergueeva, X. Zhang, A. Misra and A.K. Mukherjee, "*The effects of decreasing layer thickness on the high temperature mechanical behavior of Cu/Nb nanoscale multilayers*", Thin Solid Films 515 (6), (2007), 3241-3245
- [24] A.Sergueeva, N.A. Mara, and A.K. Mukherjee, "*Structure and mechanical behavior relationship In nano-scaled multilayered materials*", Mat. Res. Soc. Symp. Proc., 2001. 673

- [25] N. A. Mara, A. Sergueeva, A. Misra and A.K. Mukherjee, "Structure and high-temperature mechanical behavior relationship in nano- scaled multilayered materials" *Scripta Mater.*, 2004. 50(6): p. 803-6.
- [26] N.A. Mara, A. Misra, R.G. Hoagland and A.V. Sergueeva, "High-temperature mechanical behavior/microstructure correlation of Cu/Nb nanoscale multilayers. *Mater. Sci. Eng. A-Structural Materials Properties Microstructure and Processing*, 493(1-2) (2008), 274-282.
- [27] L. Kurmanaeva, H. Bahmanpour, T. Holland, J. McCrea, J.H. Lee, J. Jian, H. Wang, E.J. Lavernia and A.K. Mukherjee, "Room temperature mechanical behavior of a Ni-Fe multilayered material with modulated grain size distribution", *Phil. Mag.* 94 (2014), 31, 3549-3559
- [28] K.S. Kumar, S. Suresh, M.F. Chisholm, J.A. Horton and P. Wang, "Deformation of electrodeposited nanocrystalline Nickel", *Acta Mater.* 51 (2003), 387-405
- [29] A. Ovid'ko, "Review on the fracture processes in nanocrystalline materials", *J. Mater. Sci.* 42 (2007)
- [30] T.H. Courtney In: "Mechanical behavior of materials", McGraw-Hill Series in Materials Science in Engineering New York: McGraw-Hill, Inc.: (1990), 517-521
- [31] Y.P. Li and G.P. Zhang, "On plasticity and fracture of nanostructured Cu/X (X = Au, Cr) multilayers: The effects of length scale and interface/boundary", *Acta Mater.* 58 (11) (2010), 3877-3887
- [32] M. Zehetbauer and V. Seumer, "Cold work hardening in stages IV and V of fcc metals I. Experiments and interpretation", *Acta metal. mater.*, 41(2) (1993), 577-588
- [33] T.F. Dalla, P. Spaetig, R. Schaeublin and M. Victoria, "Deformation behavior and microstructure of nanocrystalline electrodeposited and high pressure torsion nickel", *Acta Mater.* 53 (2005), 2337-2349
- [34] Y.M. Wang, A.V. Hamza and E. Ma, "Temperature-dependent rate sensitivity and activation volume of nanocrystalline Ni", *Acta Mater.* 54 (2006), 2715-2726
- [35] H. Zhang, Z. Jiang and Y. Qiang, "Microstructure and tensile deformation of nanocrystalline Cu produced by pulse electrodeposition", *Mater. Sci. Eng. A* 517 (2009), 316-320
- [36] T. F. Dalla, H. Van Swygenhoven, and M. Victoria, "Nanocrystalline electrodeposited Ni: microstructure and tensile properties", *Acta Mater.* 50 (2002), 3957
- [37] C.D. Gu, J.S. Lian, Z.H. Jiang and Q. Jiang, "Enhanced tensile ductility in an electrodeposited nanocrystalline Ni", *Scripta Mater.* 54 (2006), 579-584
- [38] C.D. Gu, J.S. Lian, Q. Jiang and Z.H. Jian, "Ductile-brittle-ductile transition in an 13 nanometer grain sized Ni-8.6 wt.% Co alloy", *Mater. Sci. Eng. A* 459 (2007), 75-81
- [39] C. Gu, J. Lian and Z. Jiang, "High strength nanocrystalline Ni-Co alloy with enhanced tensile ductility", *Advanced Engineering Materials*, 8 (4) (2006), 252-256
- [40] C.D. Gu, J.S. Lian, Q. Jiang and W.T. Zheng, "Experimental and modelling investigations on strain rate sensitivity of an electrodeposited 20 nm grain sized Ni", *J. Phys. D: Applied Physics* 40 (2007), 7440-7446
- [41] S. van Petegem, J. Zimmermann, H. van Swygenhoven, "Microstructure and deformation in nanocrystalline Ni-Fe. Part II. In situ testing during X-ray diffraction", *Acta Mater.* 61 (2013), 5846-5856
- [42] G.J. Fan, L.F. Fu, H. Choo, P.K. Liaw and N.D. Browning, "Uniaxial tensile plastic deformation and grain growth of bulk nanocrystalline alloys" *Acta Mater.* 54 (2006), 4781

- [43] D.L. Grimmer, M. Schwartz and K. Nobe, "A comparison of DC and pulsed Fe-Ni alloy deposits", J. Electrochem. Soc. Vol. 140, No.4, 973-978
- [44] Q. Wei, S. Cheng, K.T. Ramesh, E. Ma "Effect of nanocrystalline and ultrafine grain sizes on the strain rate sensitivity and activation volume: fcc versus bcc metals", Mater. Sci. Eng. A, 381 (2004), 71-79
- [45] D. Martinez-Blanco, P. Gorria, J.A. Blanco and R.I. Smith, "Investigating the martensite-austenite transformation on mechanically alloyed FeNi solid solutions", J. Phys. Conf. Ser. 325 (2011), 0120129
- [46] T. Nagayama, Y. Mizutani, T. Nakamura and N. Shinohara, "Thermal expansion properties of Nickel-Iron alloy electrodeposits", Journal of the Surface Finishing Society of Japan, 57(10) (2006), 733-737
- [47] S. van Petegem, J. Zimmermann, S. Brandstetter, X. Sauvage, M. Legros, H. van Swygenhoven, "Microstructure and deformation in nanocrystalline Ni-Fe. Part I. Microstructure", Acta Mater. 61 (2013), 5835-5845
- [48] S. Cheng, J.A. Spencer and W.W. Milligan, "Strength and tension/compression asymmetry in nanostructured and ultrafine-grain metals", Acta Mater. 51(15) (2003), 4505-4518
- [49] J.E. Bird, A.K. Mukherjee, J.E. Dom, Int. Conf. Proc. Israel Univ. Press, (1969), p.255
- [50] R.L. Coble, J. Appl. Phys. (1963), 34, 1679 - 1682
- [51] Y.-S. Kang, J.-S.-Lee, S.V. Divinski and Chr. Herzig "Ni grain boundary diffusion in coarse-grained Fe-40 wt.% Ni alloy and comparison with Ni diffusion in the nanocrystalline alloy", Z. Metallkde. 95 (2004), 2, 76-79
- [52] Z. Shan, E.A. Stach, J.M.K. Wiezorek, J.A. Knapp, D.M. Follstaedt and S.X. Mao, "Grain boundary-mediated plasticity in nanocrystalline Nickel", Science 305 (2004), 654-657
- [53] Y.B. Wang, B.Q. Li and M.L. Sui, "Deformation-induced grain rotation and growth in nanocrystalline Nickel", Appl. Phys. Lett. 92 (2008), 011903
- [54] M. Chen, E. Ma, K.J. Hemker, H. Sheng, Y. Wang and X. Cheng, "Deformation Twinning in nanocrystalline Aluminum", Science 300 (2003), 1275-1277
- [55] H.M. Ledbetter and R.P. Reed, "Elastic properties on metals and alloys, I. Iron, Nickel, and Iron-Nickel Alloys", Journal of Physical and Chemical Reference Data, 2(3) (1973), 531-617
- [56] Raymond E. Schramm and Richard P. Reed, "Stacking fault energy of fcc Ni-Fe alloys by X-Ray diffraction line profile analysis", Metall. Trans. A, 7 (1976), 359-363
- [57] R.P. Reed and R.E. Schramm, "Lattice parameters of martensite and austenite in Fe-Ni alloys", J. Appl. Phys. 40 (1969), 3453-3458
- [58] J.L. Nilles and W.S. Owen, in "Mechanical Behavior of Materials". The Society of Metals, Japan, 1972, p. 97
- [59] M.A. Meyers, O. Voehringer and V.A. Lubarda, "The onset of twinning in metals: a constitutive description", Acta mater. 49 (2001), 4025-4039
- [60] V.L. Tellkamp, A. Melmed and E.J. Lavarnia, "Mechanical Behavior and Microstructure of a Thermally Stable Bulk Nanostructured Al Alloy", Met. Mat. Trans. A, 32 (2001), 2335-2343
- [61] M. Daly, J.L. McCrea, B.A. Bouwhuis, C.V. Singh and G. D. Hibbard "Deformation behavior of a NiCo multilayer with a modulated grain size distribution", , Mat. Sci. Eng. A, 642 (2015), 305-314
- [62] Y. Ivanisenko, L. Kurmanaeva, K. Yang and H.-J. Fecht, "Can we use kinetic analysis for

investigation of deformation processes in nanocrystalline materials?" Phys. Conf. Ser. 240 (2010), 012138

[63] G. V. Kurdjumov and G.-Sachs. Z. Physik. 64 1939), 325

[64] K.E. Harris, V.V. Singh and A.H. King, "Grain rotation in thin films of gold", Acta Mater., Vol. 46(8) (1998), 2623–2633

[65] M. Legros, D.S. Gianola and K.J. Hemker, "In situ TEM observations of fast grain-boundary motion in stressed nanocrystalline aluminum films", Acta Mater., Vol. 56(14) (2008), 3380–3393

[66] Y. Liu, L. Liu, B. Shen, W.Hu, "A study of thermal stability in electrodeposited nanocrystalline Fe-Ni invar alloy", Mater. Sci. Eng. A 528 (2011) 5701–5705

[67] L. Kurmanaeva, J. McCrea, J. Jian, J. Fiebig, H. Wang, A.K. Mukherjee and E.J. Lavernia, "Influence of layer thickness on mechanical properties of multilayered knife samples processed by electrodeposition", Materials & Design 90 (2015), 389-395

Captions:

Fig. 1: Stress strain curves of multilayered NiFe with 5 μm layer thickness depending on strain rate and temperature, a) room temperature b) at 400°C, c) temperature dependence of ultimate tensile stress. Possible d) temperature dependence of activation volume and strain rate sensitivity.

Fig. 2: SEM images of the fracture surface of multilayered NiFe: a) and b) at room temperature, c) and d) and at 400°C, the tests at both temperatures were performed with a strain rate of 10^{-4} s^{-1} , e) at 300°C, the material is partly pulled out, the regions are in the circle.

Fig. 3: a) and b): Bright field images of multilayered NiFe samples after tensile test at room temperature, the test was performed with a strain rate of 10^{-4} s^{-1} . c) and d) Dark field images of multilayered NiFe samples after tensile test at room temperature at a strain rate of 10^{-4} s^{-1} . The white arrows indicate twins. The tensile direction is parallel to the interphase between CG and NC layer. The twins are indicated by black arrows.

Fig. 4: a) cross section SEM images close to the fracture surface, the scale bar is 10 μm b) bright field TEM image close to the fracture surface after a tensile test at 400°C at a strain rate of 10^{-4} s^{-1} , pores are clearly visible, c) STEM image of the NC layer after a tensile test at 400°C at a strain rate of 10^{-4} s^{-1} , average grain is 100-150 nm, the grains are still equiaxed d) dark field TEM image after a tensile test at 400°C at a strain rate of 10^{-4} s^{-1} , e) Selected area diffraction of the nano grained area, f) selected area diffraction of the large grain area after a tensile test at 400°C at a strain rate of 10^{-4} s^{-1}

Fig. 5: Differential calorimetry measurements of NiFe alloy a) heating rate of 20 K/min was used, the second run does not show an exothermic peak, b) heating rate of 30 K/min was used, here also no exothermic peak was observed in the second run. The dotted lines indicate the determined peak temperature.

Fig.6: Schematic for the formation of the fine layers, a) during the deformation, b) after deformation. The coarse grained layer will deform first. The dislocations pile-up at the interlayer interphase since the dislocation activity in the nanograins is limited. These pile-ups cause internal stress in the vicinity (marked by the box) of the interlayer interface. This might assist grain rotation in the nanocrystalline layer which could lead to the coalescence of several grains that get elongated along the tensile direction during the further deformation process.

Figures:

Fig.1

Fig.2

Fig.3

Fig.4

Fig. 5

Fig.6