Mechanical and fracture behaviour of the three-scale hierarchy structure in As-deposited and annealed nanocrystalline electrodeposited Ni–Fe alloys

Mechanical and Fracture Behaviour of Three-scale Hierarchy Nanocrystalline Structure of Electrodeposited Ni-Fe Alloys

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Introduction

Electrodeposition is a versatile nanotechnology enabling the fabrication of a wide range of unique functional and structural nanocrystalline (nc) material foils of controlled composition, purity, grain size and thickness [1]. Since the '80s, the electrodeposition of nc Ni-Fe alloys is increasingly attracting attention in force of their potential applications to micro-electro-mechanical systems, magnetic devices and functional coatings being attested by their unique magnetic, thermal and mechanical properties [2] [3] [4] [5] [6] [7] [8]. The latter properties, normally expressed in terms of yield stress, ultimate tensile stress (UTS), and hardness, are particularly striking when compared to conventional coarse-grained (cg) counterparts (for instance, [9] [2] [10]).

However, electrodeposited nc Ni-Fe alloys, along with most nc metals and alloys fabricated using other routes (*e.g.*, powder consolidation, severe plastic deformation), suffer very low ductility or uniform elongation to fracture [11] [12] [13] [14] [15] [16]. Moreover, thermal stability is found to be another issue [10] [13] [17], often resulting in abnormal or excessive grain growth [14] [18] [19] [20] [21].

The mechanical properties were found to change whether in tensile or in compression. Specifically, the Ni-23wt% Fe alloy (2.8 mm thick) displayed 1.7 GPa yield stress and 2.6 GPa ultimate tensile stress (UTS) in compression when the applied load was parallel to the growth direction [9]. Similar results were achieved for the 3 mm thick Ni-18wt% Fe alloy, which displayed the UTS of 2.5 GPa [22]. The angle between the test load direction and the deposition growth direction played an important role on the UTS, which decreased up to 2.35 GPa when the applied load was perpendicular to the growth direction, whereas the yield stress was unchanged [9]. In tensile

condition, electrodeposited Ni-Fe alloys containing 8.5 [23], 18 [24] and 20 [14] wt% of iron displayed the UTS of 1.8, 2.0 and 1.9 GPa, respectively, indicating that the material performances markedly decreased from the compression regime to the tensile one [22]. Note that, for the nature of the electrodeposited foil, the tensile load is always applied perpendicularly to the growth direction, which according to compression experiments [9] is the weakest orientation.

An important role on mechanical properties was played by the iron content. In particular, the Ni-15wt% Fe alloy displayed the UTS value of 2.3 GPa [14] which dropped to 1.87 [25], 1.62 [2], 1.35 [12] and 1.61 [25] GPa with increasing the iron content up to 44, 50, 50 and 57 wt%, respectively. Vickers microhardness vs. iron content (0÷50 wt% Fe) curves showed that Ni-Fe alloys with 15÷20 wt% of iron displayed the highest performance [26] [27] [28], in agreement with the aforementioned tensile tests [2] [12] [14] [23] [24] [29] [25]. Electroplated nc pure Ni displayed 200 GPa Young's modulus [2], which dropped to 140 [11], 119 [2] and 100 [12] GPa for Ni-Fe alloys with 20, 50 and 50 wt% of Fe respectively, to be compared with 150 GPa of bulk cg Invar alloys [30] [31].

In general, the hardness of Ni-Fe alloys was found to increase with decreasing grain size, in accord to Hall-Petch law. However, when the grain size of Ni-Fe alloys was in the range 12-14 nm [32] [33] [28] its hardness revealed an inversion point in the Hall-Petch law. Analogous behaviour was observed for pure nc Ni [26] and other nc metals.

Considerable efforts are being spent to correlate the mechanical properties and microstructure of electrodeposited nc Ni-Fe alloys. The X-ray diffraction pattern of several Ni-Fe alloys showed that the face centred cube (FCC) crystal structure was preserved for Fe content lower than 55 wt% [10] [26] [13] [12] [27]. For such alloys, the (111) peak denoted a preferred orientation whereas the (200) peak was a reflection [10] [26] [13] [12] [27]. The increase in Fe content contributed to degrade the (200) peak [13] [34] meanwhile reducing the grain size [10] [5] [35] [34] (*i.e.*, from 20.8 nm in pure Ni to 12.7 nm in Ni-22.2%Fe alloy [26]) as well as slightly shifting (along 2θ axis) the (111) peak (*i.e.*, from 44.48° for pure Ni to 44.18° for the Ni-Fe alloy [26]) as a result of the increased lattice constant [26] [27] [36] [35] [34]. On the other hand, the actual morphology of the electrodeposited crystal structure of Ni-Fe alloys still remains a controversial issue. A columnar crystal [9] [15] [37] [38] [22] [39] or fibre [10] [35] crystal structure with a very strong out-of-plane texture was reported. Such columnar structure was also predicted by a Monte Carlo simulation of the electrodeposition kinetic in pure Ni [40].Columnar structure was associated to both (111) [9] [10] [37] [38] and (200) [34] [37] [38] peaks.

In contrast to the observed low tensile ductility of Ni-Fe alloys (*i.e.*, 1÷3 % elongations to fracture [6] [11] [12] [13] [14]), other studies reported 5 % for Ni-18wt% Fe [24], 5.5% for Ni-8.5wt% Fe [23], 6 % for Ni-15wt% Fe alloy [14], 12 % for Ni-20wt% Fe alloy [37], 15.8 % for Ni-56wt% Fe [25] and 15.3 % for Ni-38wt% Fe alloy [8]. The maximum attained compression strain was 22 % for both Ni-23wt% Fe [9] and Ni-20wt% Fe alloys [41]. However, these elongations were much lower than 40, 45 and 70 % tensile elongation displayed by the cg Invar 36 [31], cg pure Ni [13] and cg high purity Invar [31], respectively. Several factors may contribute to such unsatisfactory ductility of Ni-Fe alloys, *e.g.*, presence of internal or residual stresses, porosity, sulphur segregations and other sources of embrittlement [9] [37] [8] [42].

The thermal stability of microstructure in nc Ni-Fe alloys was highly debated. Often, the pure electrodeposited nc Ni was selected as a baseline. Several authors investigated the influence of

the annealing temperature on the grain size [10] [43] [20] [44] [18] [1] [19]. The observed grain growth regimes were discriminated by a critical annealing temperature range. Below this temperature range, grain boundary diffusion dominated, resulted in no significant grain growth [18] [1]. Conversely, above this temperature fast and abnormal grain growth occurred as it was dominated by lattice diffusion [18] [1]. Seo et al. [19] explained grain growth as a necessity of decreasing the total free energy of the initial nc Ni-Fe structure on annealing. Grain growth was anticipated by a prior abnormal grain growth [26] [19] [45] along the <111>//ND texture direction which was favourable for grain growth particularly for the as-deposited <111> oriented grains. This initial orientation-matching condition on annealing determined the dominating <111> texture of annealed Ni-Fe alloys. However, the critical temperature range depends on alloy composition. For several Ni-Fe alloys an approximate temperature range of 300-350 °C was identified [10] [43] [20] [44] [18] [1] [46]. Alternatively, DSC measurements [10] [19] indicated different annealing temperature which were sensitive to grain growth, *i.e.*, 280 °C for pure Ni [47], 339 °C for pure Ni [10], 392 °C for Ni-36wt% Fe [19], 398 °C for Ni-18.5wt% Fe [10], 405 °C for Ni-50wt% Fe [19] and 424 °C for Ni-57wt% Fe alloys [19]. Thus, using DSC analysis [10] [19], the higher the Fe content, the higher the critical temperature. This means that the presence of Fe in the lattice increased the thermal stability of the alloys [10]. Although the heating rate may markedly influence the measurement of the critical temperature [48] [49].

For annealing temperatures just below the critical range (*e.g.*, 250 [9] and 300 [37] °C) the mechanical performance of annealed nc Ni-Fe alloys generally improved in both compression and tension owing to a beneficial closure of porosities [9] [37], relaxation of internal stresses [10] [18] [1] and negligible grain growth [1]. Conversely, for temperatures either above or much above the critical range (say, from 400 to 600 °C [37]), a drop in the tensile properties was observed [37]. In the limit, for temperatures from 700 °C to 1150 °C, the mechanical behaviour of annealed nc Ni-Fe alloys followed that of conventional cg alloys. Specifically, the tensile strength fell off drastically and the fracture strain markedly increased [11] [12]. Incidentally, such direct relationship between grain size and annealing temperature, can be alternatively exploited in practice to control the final mechanical properties of electrodeposited Ni-Fe alloys as grain size can be varied from few nm to hundreds of μm. Despite this, several authors reported [26] [19] [45] [50] [51] an abrupt increase in grain size of Ni-Fe alloys just above the upper limit of the critical range. The reason for such unique behaviour is still unclear and demands further investigation.

On the other hand, the fracture behaviour of nc Ni-Fe alloys has been relatively overlooked [17]. It was found that the grain size markedly influenced the failure behaviour of the nc Ni-Fe alloys [17]. Sufficiently large grains allowed the generation and migration of dislocations leading to ductile fracture, such as in the case of pure Ni with 44 nm average grain size [17]. The fracture surfaces of single-phase nc metals (*e.g.*, pure Ni) displayed a cup-cup pattern due to microvoid coalescence, being indicative of a ductile fracture [17]. Conversely, when the average grain size was very small (*e.g.*, 7 nm for Ni-15wt% Fe alloy) the generation and migration of dislocations inside the crystals was inhibited whereas grain boundary sliding was enhanced [17]. Failure occurred under tensile test without any macroscopic necking although plasticity prior to failure occurred to some extent. Indeed, fracture surface exhibited a peculiar “void-like” morphology. The authors explained such fracture behaviour as resulting from the break of atomic bonds along a path that created cups and cones [17].Thus, the fracture behaviour was denoted by the authors as of brittle type [17].

Despite the considerable amount of results collected so far on electrodeposited nc Ni-Fe alloys, our understanding on the basic phenomena governing strength, ductility and fracture in relation to microstructure is still lacking for both as-deposited and annealed alloys. Thus, the primary aim of this paper is to study the structural, mechanical and fracture characteristics of an electrodeposited

nc Ni-48wt% Fe alloy before and after annealing across the 300 ÷ 400 °C range up to 800 °C. The second aim is to define a correlation between the mechanical properties and microstructure through inspection of the intricate nanoscopic features of the electrodeposits' microstructure.

Materials and Methods

Nc Ni-48wt% Fe alloy foils were produced by electrodeposition [52]. An AISI 304 stainless steel (cathode) and a Ni plate (anode) were used as electrodes. The electrolyte bath contained iron chloride and nickel sulfate. Saccharine was added as grain refiner and stress reliever [53] [54] [55] [56]. The electrodeposition process was conducted under DC condition using a constant current density of 60 mA cm^{-2}. First, a Ni-Fe alloy film was deposited over the cathode substrate up to 100±5 or 200±10 µm in thickness. It was then mechanically stripped into a free-standing foil. The chemical composition across the thickness of the foils, measured by energy dispersive X-ray spectrometer (EDX, Quantax 200, Bruker), deviated within the 4 % with respect to the nominal composition. The mechanical properties versus grain size in the nc foils were changed by annealing heat treatment in a N_2+H_2 atmosphere at temperatures across the critical range (say, 300, 320, 350, 370 °C) up to 800 °C, under a heating rate of +5 °C/min and 60 min holding.

Possible impurities in the foils (*e.g.*, S and P) were inspected using inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 8300, Perkin Elmer).
The crystal structure is of primary concern to explain the mechanical properties of the electrodeposited nc Ni-Fe alloys. X-ray diffraction analysis were performed with X-ray diffractometer (XRD, D8 Discover, Bruker) using 1.54 Å wavelength. The Scherrer's equation was applied to the diffraction peaks to estimate the average grain size (*D*) of each foil:

$$D = \frac{0.9\,\lambda}{\beta\,\cos\theta} \qquad \text{Eq. 1}$$

where λ is the X-ray wavelength, β and θ are the full width at the half-maximum and diffraction angle of each selected peak respectively.
The spacing of (111) and (200) planes (d_{111} and d_{200}, respectively) were measured using the Bragg's equation:

$$2\,d\,\sin\theta = n\,\lambda \qquad \text{Eq. 2}$$

where *n* is a positive integer. The lattice parameter (a_{FCC}) was estimated as follows [18]:

$$a_{FCC} = \sqrt{3}\,d_{111} \qquad \text{Eq. 3.a}$$

$$a_{FCC} = 2\,d_{200} \qquad \text{Eq. 3.b}$$

The tensile properties of the as-deposited and annealed foils were measured at room temperature by a universal testing machine (UTM, Instron 5569) coupled with a video-extensometer under a strain rate of 0.5 mm min^{-1}. The samples were of dumbbell-shape type [8] having a 10 mm gauge length and 100 µm in thickness. Indentation properties were tested on 200 µm thick foils using a Berkovich indenter, under load control mode, by means of nano-instrumented indenter (Hysitron

Triboindenter, Bruker). The maximum load (1 mN) was held for 10 s. The loading/unloading rates were constant and equal to ± 50 µN s^{-1}. Each indentation test was repeated ten times. The Oliver-Pharr method [57] was applied to extract the indentation modulus (E_{IT}) and hardness (H_{IT}). To compare the mechanical strength from uniaxial tensile test and nano-instrumented indentation test (nIIT) the Tabor *reference flow stress-strain* rule [58] was adopted. It states that the reference flow stress (σ_{rf}) is given by:

$$\sigma_{rf} = \frac{H_{IT}}{3} \qquad \text{Eq. 4}$$

Typical indentation imprints in the as-deposited and annealed at 370 °C foils were observed using the atomic force microscopy (AFM, Hysitron Triboindenter, Bruker) by imposing a 10 mN maximum load.
To prevent undesired indentation size effects (ISE) prior nIIT experiments were conducted at different peak loads to assess uniformity in hardness with depth. This condition was achieved by ensuring the maximum indentation depths greater than 50 nm. The corresponding ISE-free peak load found was then set for actual nIIT experiments. This procedure was supported by Such et al.'s results [32], who reported a successfully achieved uniformity in hardness measurements in pure Ni with maximum indentation depths in the range of 50 to 300-500 nm.

The microstructure morphology of the Ni-Fe alloy deposits was analyzed using field emission scanning electron microscopy (FESEM) before and after annealing as well as over either polished and etched or fracture surfaces. The latter was intentionally induced by causing an oblique fracture surface under bending loading. One half of the sample was fixed in the grips while the other half end was bent about a pre-cut notch. Conventional etching of nc Ni-Fe foils failed as they exhibit excessively high surface reactivity. However, it was determined by a trial-and-error procedure that the exposure of nc foils at room temperature to aqua-regia vapour for 30 min gave satisfactory results for both as-deposited and annealed samples.

Experimental Results

ICP-OES analysis on the as-deposited foils did not detect any significant presence of P but the content of S was as low as 409.41 ppm.
Figure 1 shows the X-ray diffraction spectra of the as-deposited and annealed samples at the various annealing temperatures. The FCC phase was dominant in all Ni-Fe samples. The (111) and (200) peaks [10] [26] [13] [12] [27] denoted the preferred orientation and reflection respectively. Both peaks shrunk with increasing temperature [26] [12], although the latter also contracted in intensity. Note that the relative peak height of the (111) and (200) peaks did not remarkably change up to 370 °C. Above 375 °C, a significant relative contraction of the (200) peak was detected. Based on the Scherrer's law (Eq. 1), a shrinkage in the XRD peak corresponds to an increase in average grain size, as confirmed in Figure 2. Note that the peak shrinkage in XRD spectra has also been shown to associate with a decrease in internal strain (or stress) [35] [59]. Accordingly, the estimated grain size, for both leading orientations is plotted against the annealing temperature. For convenience, the average grain size is also reported in Table 1 which is introduced to summarize the present and following results for the as-deposited and annealed samples.

The average grain size remained unaltered below 320 °C but suddenly increased above 320 °C. The growth rate lowered at slightly higher temperature such as 350 and 370 °C, hence confirming the observed critical behavior of nc Ni-Fe about the critical range [10] [43] [20] [44] [18] [1] [46].
The lattice parameter was estimated (Eqs. 3.a and 3.b) as 3.59 Å for the as-deposited alloy, which is in good agreement with other studies [18] [36] [60] [35] [8] [61].
Tensile stress-strain curves before and after annealing are shown in Figure 3. The *post-mortem* samples are shown in Figure 4. The values of tensile properties are summarized in Table 1 for the as-deposited and annealed samples. The stress-strain curve at 350 °C was omitted in Figure 3 due to accidental slip bending (no fracture) of the sample during testing. Incidentally, the uniaxial tensile test for 350 °C was repeated three times more. However, in all cases it exhibited a tensile fracture between the grips and thus finally neglected.

Table 1: grain sizes and mechanical properties of as-deposited and annealed foils at different annealing temperatures.

Annealing Treatment	Grain Size / nm			Uniaxial Tensile Test				nIIT		
	(111) peak	(200) peak	Av.	E GPa	σ_Y MPa	UTS MPa	ε_{MAX} %	E_{IT} GPa (%*SD*)	H_{IT} GPa (%*SD*)	σ_{rf} GPa (%*SD*)
as-Deposited (1)	9	5	7.0	106	1144	1389	2.22	119 (5)	5.4 (3)	1.8 (3)
as-Deposited (2)				129	991	1044	0.83			
300 °C	10	5	8.5	127	1425	1808	3.22	-	-	-
320 °C	13	11	12	-	-	-	-	133 (3)	6.5 (4)	2.2 (4)
350 °C	14	12	13	-	-	-	-	144 (3)	6.8 (2)	2.3 (2)
370 °C	15	14	14.5	162	877	1090	1.96	145 (5)	6.6 (3)	2.2 (3)
400 °C	-	-	-	-	764	880	1.40	-	-	-

The tensile behavior of the as-deposited samples was repeated twice, confirming its tensile reproducibility. Surprisingly, the largest elongation-to-fracture and UTS were achieved for the 300 °C annealed sample. All samples fractured within the gauge length, except for just the 300 °C annealed sample. The FESEM images of the tensile fracture surfaces of the as-deposited and annealed at 300 °C are shown in Figures 5.a and 5.b. Figure 6 is the FESEM planar view of the *post-mortem* as-deposited sample near the tensile fracture surface. As per the mode of fracture, it must be anticipated that, according to FESEM observations, all fracture surfaces were ductile-like on nanoscopic scale, due to the presence of dimple features (not shown). By contrast, inspection of the macroscopic outline of the fracture surfaces and of the low angle between the fracture surface and the load direction, suggested that the fracture was of brittle nature on macroscopic scale.
The Young modulus increased with increasing annealing temperature. Yield stress, UTS and fracture strain attained a maximum for the 300 °C annealed sample. Upon bending, the fracture behaviour of the as-deposited foils was again likely ductile in nature. Conversely, the annealed foils were increasingly brittle with increasing annealing temperature up to 370 °C [13].
Figure 7 compares the tensile properties of present as-deposited alloy against other electrodeposited Ni-Fe alloys of similar contents of iron from literature [2] [11] [12] [25]. The yield stress and Young modulus compared well in the case of Ni-50wt% Fe alloys [2] [12] (Figure 7) whereas the UTS matched with only one corresponding literature value of a similar Ni-50wt% Fe alloy [12] (Figure 7). By contrast, the measured UTS value was slightly lower than those presented in other studies for three alloys of similar iron content, namely, 44 [25], 50 [2] and 57 wt% Fe [25] (Figure 7).

The load-displacement curves from nIITs for the as-deposited and annealed samples are shown in Figure 8. For clarity, each sample is represented by only three (rather than ten) indentation curves corresponding to the maximum, minimum and averaged maximum penetration depth, respectively. The indentation modulus, hardness, reference flow stress and inherent associated standard deviation (%SD) are summarized in Table 1. Figure 9.a and 9.b show the AFM scans of two Berkovich nanoimprints for the as-deposited and annealed sample at 370 °C, respectively.

The measured indentation hardness values are depicted in Figure 10 as a function of the measured average grain size. For sake of comparison, the figure also includes the corresponding values of the nanoindentation hardness of pure Ni [32] and the micro-Vickers hardness of Ni-Fe alloys (the Fe content ranges from 0 to 29 wt%) [26]. The hardness of the present alloy achieved its maximum at 13 nm, in accord with other studies [26] [32]. However, it is necessary to stress that the hardness values in Figure 10 were associated to grain sizes having different meaning. Specifically, our own hardness vs. grain size points derived from an increase in annealing temperature of the given as-deposited Ni-48wt% Fe alloy, whereas the respective points taken from literature refer to different as-deposited Ni-Fe alloys from different deposition conditions [26] [32]. By using such prior assumption, we noticed that all the aforesaid hardness-grain size points reproduced a common trend qualitatively [26] and quantitatively [32].

For a more in-depth inspection of the fracture behaviour of the as-deposited nc Ni-48wt% Fe alloy, an intentional oblique bending fracture was performed across the thickness of the foil (see the inset in Figure 11). The FESEM image of the resulting cross-sectional view of the oblique fracture surface is shown in Figure 11. The microstructure exhibited a general columnar grain morphology as evidenced by the fibers along the growth direction. The applied loading solicited the columnar grains (fibers) in tensile by culminating in a special cup-cone mode of fracture. The cups locate in the top whereas the cones in the bottom of the figure. Interestingly, the diameter of the spherical cups and cones was within a well-defined range of 155-165 nm. This peculiar cup-cone fracture morphology suggests that the as-deposited Ni-Fe foils fail in ductile mode at the nanoscopic scale but in brittle mode at macroscopic scale, as confirmed by the tensile samples.

Figure 12 shows a FESEM image along the cross-section of the as-deposited foil after mechanical polishing and vapour etching. The structure of the elongated grains along the growth direction was confirmed. The dashed lines (white) are traced along the outline of the columnar grains suggesting that they can possess different sizes. The etching made evidence of an interesting feature of the elongated grains being that of consisting of aggregates of spherical grains. The average diameter of these spherical grains was just in the range of 155-165 nm. This was closely related with the diameter of the smallest columnar grains which was also in the range 155-165 nm. Accordingly, we may define 155-165 nm as a characteristic grain size range and the spherical grains as characteristic grains. Moreover, etching also revealed a copious presence of spherical pores, in addition to deposition pores. It was difficult after etching, to clearly discern between etching porosity and deposition porosity. FESEM images suggested that etching porosity resulted from chemical reactions with other sources of defects, impurities, segregations, etc. whereas the deposition porosity was induced by gas entrapment during electrodeposition.

Figures 13.a and 13.b are FESEM images of the top view of the deposit after vapour etching. Depending on the cutting plane of the etched surface, the columnar grains (and thus its characteristic grains) could be cut at different diameters which may range from ~50 to ~250 nm. A

further interesting feature shown in Figures 13.a and 13.b was the "*nested three-modal structure*" of the columnar grains. Embedded in the characteristic grains (as visible in cross section), a narrow distribution of nanoscopic equiaxed grains was observed. However, we could not measure the size of the nc grains precisely by FESEM, even at 500 kX, because of their very tiny size. We can guess their average size to be smaller than 20 nm.

Thus, in summary, the elongated grains, developed during deposition, included clusters of characteristic spherical grains which, in turn, were composed of nanocrystalline grains. In the top-view images of Figures 13.a and 13.b, the electrodeposited Ni-Fe 48 wt% Fe alloy structure appeared as a three-level nested microstructure made of nc grains embedded in the characteristic spherical grains of 155-165 nm average grain size and these, in turn, composed the columnar grain. The latter were easily recognized since often their boundaries were populated by deposition defects such as pores or segregations (see the inset in Figure 13.b). Conversely, no perceivable defects were generally appreciated between neither nanoscopic grains nor characteristic grains unless a columnar grain degenerated in one single characteristic grain. A schematic view of the electrodeposited nc Ni-Fe alloy microstructure is sketched in the inset in Figure 13.c (see Discussion section).

Discussion

The typical columnar structure of electrodeposited foils was previously reported for both pure Ni [10] [35] [38] [39] [40] and Ni-Fe alloys [9] [10] [15] [22] [35] [37] and it was associated to both (111) [9] [10] [37] [38] and (200) [34] [37] [38] texture in the case of FCC crystals. In this work, the microstructure of the as-deposited Ni-48wt% Fe is composed, on the nanoscopic scale, of very fine defect-free equiaxed nc grains of smaller average grain size than 20 nm (Figures 13.a and 13.b). Such qualitative estimate compares well with the more quantitative value of 7 nm estimated from XRD peaks (Table 1). By cross-linking XRD data with FESEM information from the front view and cross-section images of the foil the likely resulting microstructure appears as shown in the inset c of Figure 13.

The columnar grains, bounded by their own columnar grain boundaries (thick lines), grow along the deposition direction and embed one or more characteristic equiaxed grains. The latter, in turn, are delimited by their characteristic grain boundaries (thin lines) and embed the nc grains. The actual columnar grains may be somewhat inclined (up to 10° [9]) and consisting of multiple bonded sub-columnar grains [22]. The resulting film structure, as anticipated, is a three-level nested microstructure with high expected anisotropic properties depending on the loading direction. Such deposited microstructure of the Ni-Fe foils can be compatible with a transition from a columnar structure into a cellular structure, *e.g.*, due to local changes in chemical (*i.e.*, Ni, Fe) composition, the size of the resulting cell coinciding with the size of the characteristic grain. The latter is determined by the deposition conditions (current density, temperature and electrolyte, etc.).

At first glance, the cup-cone fracture morphology observed from the bending fracture (Figure 11) would suggest a ductile fracture at least on nanoscopic scale. A unique feature highlighted by FESEM is that the average diameter of such cup-cones always ranges from 155 to 165 nm whereas the diameter of the columnar grains ranges from 50 to 250 nm depending on the selected cutting plane. The two observations match to each other since the columnar grains are composed of characteristic

spherical grains of just 155-165 nm in diameter. Upon intentional bending (*i.e.*, tensile along the growth direction of the fiber) the columnar grains fail across their cross section. The bonding strength between the characteristic grains via their grain boundaries becomes crucial. This mode of loading has shown that the strength between characteristic grains is lower than between nc grains. The fracture by longitudinal shear among fibers is even less likely. Incidentally, analogous spherical grains were also reported in the case of electroplated pure Ni (see Figure 10 in [62]) and Ni-50wt% Fe alloy foils (see Figure 2.a in [12]). In the former study [62] such grains were defined as "*cluster of nc grains*", however, they were neglected in the latter [12].

On the other hand, the uniaxial tensile test solicits the fiber perpendicularly to their growth direction, as sketched in Figure 4. Tensile test results show that this direction is more critical for the foil as the bounding strength of the columnar grains is usually weakened by deposition defects. Compression experiments attested that both UTS and fracture elongation fell off when the compression load was perpendicular to the growth direction of the fibers [9]. The inspection of fracture surface by tensile test of our as-deposited samples (Figures 5.a and 6) confirm that its morphology is very similar to that of a Ni-15wt% Fe alloy [17] [63]. On a macroscopic viewpoint, the fracture surface is characterized by deformation bands and microcracks (see Figure 6). Failure is likely to occur because of the coalescence and propagation of such microcracks [63]. In agreement with refs. [17] [63] we classify the fracture behaviour of as-deposited Ni-Fe alloy foils from tensile test as brittle-like, being preceded by a limited plastic deformation before fracture.

Notice that a cup-cone (or void-like) structure [17] was also reported in the case of the fracture surface by tensile test of Ni-15wt% Fe alloy. The cups and the cones were considerably larger than the nc grains in agreement with the present observations. However, the authors associated such a cup-cone morphology to the breaking of atomic bonds due to the intergranular propagation of the crack and classified this failure as brittle [17].

Thus, based on present results and previous investigations [17] [63] we may summarize that the fracture behaviour of as-deposited FCC Ni-Fe alloys depends on the manner which the foils are loaded, namely, ductile on nanoscopic level then the fibers are loaded along their growth direction (as in bending test) and brittle-like when the fibers are loaded transversally (as in uniaxial tensile test). The latter character prevails on a macroscopic scale as porosities and deposition defects at grain boundaries of either columnar or characteristic grains are dominant factors of brittle fracture.

Worth to mention is that such anisotropic behaviour in fracture of as-deposited Ni-Fe alloy foils inevitably reflect on the measured mechanical properties. Thus it is of paramount importance to clarify the direction of load with respect to growth direction of fibers. It is just the combination between alignment of fibers vs the test load and minimization of critical size and content of deposition defects that determine the strength and elongation to fracture of as-deposited Ni-Fe alloys foils. Among the various deposition defects, FESEM images show after vapour etching relatively large porosities prevalently at columnar grain boundaries. We attribute these to H absorption which among other cause severe embrittlement of the foils. Annealing of as-deposited foils at 300 °C might explain the improved mechanical properties due to the desorption of H. Moreover, annealing caused stress relieving [10] [18] [1], closure of the porosities [9] [37] and a change in the crystal structure.

The grain size of as-deposited foils along the (111) orientation is larger than that along the (200) orientation (Table 1 and Figure 2). Upon annealing at 300 °C both oriented grains hardly grow but grow fast from 300 to 370 °C by approaching the same grain size. Note that, the growth rate of the (200) oriented grains is significantly higher than that of the (111) oriented grains, in agreement with ref [10] for Ni-18.5wt% Fe alloy.

When the as-deposited Ni-48wt% Fe was annealed at 300°C the mechanical properties improved, as shown in Figure 3 and Table 1, with no significant change in nc grain size. Namely the yield stress and UTS increased in agreement with other studies ([9] [37] and [37], respectively). Moreover, we have found that the tensile ductility has markedly increased as well. The increase in yield stress and UTS can be attributed to the favourable closure of the porosities [9] [37] which make the role of available dislocations (very high in density in the as-deposited foil [64] [65] [66] [67] [68]) more profitable in terms of strain hardening and elongation to fracture with increasing temperature. The increase in ductility can be also ascribed to stress relieving [10] [18] [1]. The fractography of Figure 5.b shows a clear ductile fracture surface in the case of the 300 °C annealed sample, which differs from Figure 5.a relative to the as-deposited sample. This behaviour might be attributed to the desorption of H at high temperature which improved the mechanical properties. Although, still a certain amount of H remains in the sample. At higher temperatures, H may be considered as completely desorbed but the abrupt grain growth of nc grain, which starts from 300 °C and continues growing to upper temperatures, become the main cause of embrittlement. Indeed, on increasing the annealing temperature to 370° and 400 °C, a continuous drop in the yield stress, UTS and tensile ductility is observed. Expectedly, a drastic reduction of deposition dislocations is consequent to increase in annealing temperature, as proved by the reduced strain hardening ability of the annealed samples and reduced strain to fracture.

Hardness tests deviate somewhat from tensile test with increasing annealing temperature. Hardness increases with increasing temperature up to 350-370 °C (6.8 GPa). Such a different behaviour can be associated to the anisotropic behaviour of the foil with respect to different loading direction (*i.e.*, either tensile or compression).

In general, the σ_{rf}, according to its definition [58], locates between the yield stress and the UTS of the isotropic materials. However, the estimated σ_{rf} values seem to be in excess when compared with UTS data for the as-deposited and annealed samples. Conversely, σ_{rf} values compare well with the yield stress and UTS measured in compression tests [9] [14]. As the nIITs were performed on the plane of the foils, the applied load was aligned with the growth direction of the columnar structure which is expected to be the strongest direction [9]. The discrepancy between σ_{rf} and UTS in this study suggests that the foil strength is higher when loaded normally to the plane in agreement to ref. [9]. Notice that indentation test sensed the foil in pure compression in a small region of the deposit, *i.e.*, along the columnar direction of the fibers, with minimal, if not negligible, detrimental influence of deposition defects along grain boundaries. We consider that this kind of loading of the anisotropic structure of the foil is presumably the main reason for the relatively large hardness commonly reported in electrodeposited Ni-Fe alloys. It is not clear at present whether the large elastic recovery on unloading at relatively low load has to be ascribed to a spring effect promoted by an initially bent thin film (e.g., induced by residual stresses), or to an on-loading bending or to an intrinsic stiffness of the foil structure. To exclude the former factor, future experiments should investigate in more detail the final elastic recovery on nIIT unloading in foils of different thicknesses.

According to literature [2] [11] [12] [61], the Young's modulus (Figure 7) of the as-deposited alloys decreases with increasing the Fe content. In this study, we measured 118 GPa for the Ni-48wt% Fe which compares well with 99 [2] and 119 [12] GPa for two Ni-50wt% Fe alloys. The measured Young's modulus also agrees with estimated indentation modulus, as shown in Table 1. The indentation hardness and modulus (Table 1) are very similar to 5.7 and 130 GPa respectively in the case of the Ni-64wt% Fe alloy [3]. Both uniaxial tensile test and nIIT indicated an increase of the elastic properties as a function of the annealing temperature in agreement with nc pure Ni observations [69]. A similar behaviour was observed in nc Cu and Pd, for which the increased elastic modulus was associated to the reduced porosity upon annealing [70]. Moreover, by comparing the elastic tensile ranges of the as-deposited and annealed samples reported in ref. [9], we notice a slight increase in the elastic modulus after annealing, which agrees our uniaxial tensile test and nIIT measurements.

Conclusions

The electrodeposition of Ni-48wt% Fe alloy in thick foils originated a *three-level nested* grain structure, from the nc scale (order of 10 nm) to the larger columnar grain scale (up to 250 nm) passing from an intermediate uniform grain structure, denoted as characteristic grain structure, being in the range of 155-165 nm. Such high anisotropy of the nested nc structure was felt to be main the reason for the unique mechanical strength and hardness of electrodeposited Ni-Fe alloys.

Deposition defects (*e.g.*, porosities and segregations) were mainly located at either columnar grain boundaries or characteristic grain boundaries and played a major role on tensile ductility. Porosities were mostly attributed to H trapping (as gas or hydrates), while segregations were of S type.

Tensile tests showed that the mechanical properties of the as-deposited foils were lower than those at 300 °C, reaching the highest at this temperature whilst progressively falling off with increasing temperature above 300 °C. The enhanced mechanical properties at 300 °C could be explained because of both the beneficial closure of deposition porosities and H desorption. The marked increase in tensile elongation to fracture at 300 °C was in contrast with literature. The rapid drop of mechanical properties above 300 °C could be ascribed to excessive grain growth thereby making the role of grain boundary defects more critical especially in tensile testing.

The elastic properties, namely, the indentation modulus and Young's modulus did not display any dependence from the columnar structure of the foils.

The high anisotropic structure of the electrodeposited foils did not allow a sound comparison of tensile properties and indentation properties owing to the different role played by defects under the two distinct loading directions. Tensile loading was most severe, as columnar grain boundary defects operate under opening fracture mode. Bending loading, on the other hand, permitted to sense the pure plastic behaviour of the columnar grains, showing a characteristic cup-cone morphology in bending (oblique) fracture condition.

Compliance with ethical standards

We state that there is no conflict of interest.

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