Nanotwin-assisted nitridation in FeNi nanopowders for synthesis of rare-earth-free magnets

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Research Article

Keywords: phase, feni. transformation, ordered, applications, synthetic

Posted Date: November 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1089839/v1>

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Abstract

L10-ordered FeNi alloy (tetrataenite), a promising candidate for rare-earth-free and low-cost permanent magnet applications, is attracting increasing attention from academic and industrial communities. Highly ordered single-phase L10-FeNi is difficult to synthesize efficiently because of its low chemical order-disorder transition temperature (200–320 °C). A non-equilibrium synthetic route utilizing a nitrogen topotactic reaction has been considered a valid approach, although the phase transformation mechanism is currently unknown. Herein, we investigated the basis of this reaction, namely the formation mechanism of the tetragonal FeNiN precursor phase during the nitridation of FeNi nanopowders. Detailed microstructure analysis revealed that the FeNiN precursor phase could preferentially nucleate at the nanotwinned region during nitridation and subsequently grew following a massive transformation, with high-index irrational orientation relationships and ledge-wise growth motion detected at the migrating phase interface. This is the first report of a massive phase transformation detected in an Fe-Ni-N system and provides new insights into the phase transformation during the nitriding process. This work is expected to promote the synthetic optimization of fully ordered FeNi alloys for various magnetic applications.

Introduction

Permanent magnets are an integral part of the modern world and are indispensable in many critical technologies, including high-efficiency motors and generators, and medical equipment^{1,2}. Current state-of-the-art permanent magnets mostly contain rare earth elements (Nd/Sm/Dy/Pr/La) owing to their high maximum energy product. However, such expensive, strategic, and insecure resources have raised severe concerns owing to their availability, extraction difficulties, and national security^{3,4}. Thus, significant efforts have been made to develop alternative advanced rare-earth-free permanent magnets that deliver the same performance as rare-earth magnets, or at best exhibit an equal cost performance capability⁵. Tetragonal L10 FeNi (tetrataenite) is drawing considerable attention as a promising candidate for rare-earth-free permanent magnet materials⁵⁻⁷, owing to a high uniaxial magnetic anisotropy (0.6–1.3 MJ m⁻³), sufficiently large saturation magnetisation (1.6–1.65 T), and composition consisting of earth-abundant elements. Because of its low chemical order-disorder transition temperature (200–320 °C), the synthesis of single-phase, highly L10-ordered FeNi alloys through conventional thermally activated processes is extremely challenging. Several attempts have been made to promote low-temperature atomic diffusion^{8,9} and/or directly fabricate L10-ordered FeNi films via alternate monatomic layer deposition^{10,11}. Recently, Goto et al. utilized a novel approach and artificially synthesised a L10 FeNi with the highest reported degree of chemical ordering ($S \sim 0.71$) through nitrogen topotactic extraction from FeNiN powders¹². However, bulk synthesis with a large volume fraction of the fully L10-ordered FeNi phase has not been achieved in any laboratory to date. Thus, further fundamental studies on the metallurgical processing, phase formation, and microstructural changes to obtain ordered FeNiN precursor phase are essential, especially for the development of bulk L10-ordered FeNi alloy-based permanent magnets. Figure 1 illustrates a typical nitrogen topotactic reaction synthetic path¹² from FeNi

random alloy (A1-FeNi) (Fig. 1a) to the final L10-ordered FeNi alloy (Fig. 1f), with the corresponding crystal model and calculated relative formation energy for each phase. The energy levels were calculated based on the ordered state of FeNi and the isolated N₂ molecule (see Methods). The randomly disordered FeNi (A1-FeNi) alloy (Fig. 1a) is first nitrided into a partially randomly disordered Fe₂Ni₂N alloy (Fig. 1b), that is, until 1/4 of the octahedral sites are occupied by the nitrogen atoms and nickel atoms take the core sites. However, since the energy difference between the randomly disordered Fe₂Ni₂N phase and the ordered Fe₂Ni₂N (Fig. 1e) is only 124 meV, which appears too small to be the driving force behind the dynamic movement of metal atoms to fully order. Further nitriding Fe₂Ni₂N may lead to the formation of randomly disordered FeNiN alloy (Fig. 1c) with a much higher energy (522 meV vs. L10-FeNi). Energy of FeNiN with L10 type order (Fig. 1d) is, on the other hand, 437 meV lower than the random state, which seems to be a driving force for rearrangement of metal atoms. It is considered that a high-energy over-nitriding state, such as the randomly disordered FeNiN, can appear locally and temporarily on the particle surface or grain boundary of Fe₂Ni₂N under a certain condition. Then, local rearrangement of metal atoms occurs as a route to reduce the energy of the system. The reaction process from random Fe₂Ni₂N to ordered FeNiN alloy is therefore expected to be extremely slow, which is consistent with the experimental results. Once an energetically stable FeNiN phase with a L10 type order is established macroscopically, L10-ordered FeNi (Fig. 1f) is readily obtained by the nitrogen topotactic extraction, considering that the metallic atom arrangement of ordered FeNiN is identical to that of L10-ordered FeNi. As demonstrated with Fig.1, the most critical and time-consuming part of the nitrogen topotactic reaction route is related to the formation of the ordered FeNiN precursor phase. Therefore, in this work, we systematically studied the formation mechanism of the FeNiN precursor phase during the nitridation of FeNi nanopowders through detailed microstructure analysis. The results indicate a massive phase transformation from the random Fe₂Ni₂N to the ordered FeNiN phase, which is the first reported experimental demonstration of such an interface-controlled phase transformation in a Fe-Ni-N material system. This work provides valuable insights into the fundamental understanding of the phase transformation during nitridation, which may also promote further optimisation for the development of L10-ordered FeNi-based rare-earth-free permanent magnets.

Results And Discussion

Microstructure evolution during nitridation. The FeNi nanopowders (NPs) were synthesised using a novel low oxygen induction thermal plasma (LO-ITP) system. The as ITP synthesized NPs were then reduced under a hydrogen gas flow to remove the possible oxide surface. Finally, the FeNi NPs were nitrided under an ammonia gas flow (see **Methods**). To investigate the formation mechanism of the FeNiN precursor phase in the FeNi NPs during nitridation, we conducted a detailed microstructure analysis of NPs in an intermediate state, that is, a mixture of the Fe₂Ni₂N parent and FeNiN product phases. **Figure 2a,b** shows the morphology with scanning electron microscopy (SEM) images of the as ITP processed and nitrided FeNi NPs, respectively. Over 500 NPs were counted for the particle size distribution (insets in Fig. 2a,b), and the mean particle size is approximately 116.9 ± 72.6 and 99.8 ± 53.2 nm for the as ITP processed and nitrided NPs, respectively. Figure 2c presents the X-ray diffraction (XRD) patterns of (i) as ITP

processed and (ii) nitrided FeNi NPs. As indicated, the as ITP processed FeNi NPs possess a single A1-FeNi phase, whereas the nitrided FeNi NPs show a mixture of $\text{Fe}_2\text{Ni}_2\text{N}$ and FeNiN phases. Rietveld analysis using the RIETAN-FP software¹³ revealed approximately 80% of the $\text{Fe}_2\text{Ni}_2\text{N}$ phase and 20% of the FeNiN phase in the nitrided FeNi NPs. Such an intermediate state with mixed phases during nitridation can serve as a suitable material platform for investigating the formation mechanism of the FeNiN precursor phases.

Nucleation of the FeNiN phase in the nanotwinned region. To investigate the formation mechanism of the FeNiN precursor phase, it is important to first identify where and how the FeNiN phase is distributed in the nitrided FeNi NPs. Since $\text{Fe}_2\text{Ni}_2\text{N}$ and FeNiN phase belongs to space groups with distinct lattice symmetry (Pm-3m and P4/mmm for the $\text{Fe}_2\text{Ni}_2\text{N}$ and FeNiN phase, respectively) and have different lattice constants ($a = 0.377$ nm for the $\text{Fe}_2\text{Ni}_2\text{N}$ phase vs. $a = 0.400$ nm, $c = 0.371$ nm for the FeNiN phase). Thus, it is possible to distinguish between the two phases using transmission Kikuchi diffraction (TKD) analysis. **Figure 3a,b** show the TKD image quality and phase maps, respectively. The clear colour contrast in the TKD phase map (Fig. 3b) confirms a mixture of the FeNiN (red) and $\text{Fe}_2\text{Ni}_2\text{N}$ (green) phases in the nitrided FeNi NPs, which is consistent with the XRD results (Fig. 2c). Interestingly, as indicated by the white arrows in Fig. 3b, the FeNiN and $\text{Fe}_2\text{Ni}_2\text{N}$ phases in the nitrided NPs generally share sharp/straight boundaries.

Another approach considered to distinguish between the FeNiN and $\text{Fe}_2\text{Ni}_2\text{N}$ phases is the different nitrogen concentration in the $\text{Fe}_2\text{Ni}_2\text{N}$ (20.0%) and FeNiN (33.3%) phases. Specifically, the visible contrast between the electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) mapping of nitrogen can help accurately identify where and how the FeNiN phase is distributed in the nitrided FeNi NPs. Figure 3c,d show the representative EELS maps of the nitrided FeNi NPs, marked as “B” in Fig. 3a. With a high sensitivity to the light elements, the EELS map of the nitrogen distribution in Fig. 3d shows that the left part of “B” has a relatively higher nitrogen concentration than the remaining right part, sharing a boundary which is consistent with the TKD phase map in Fig. 3b. Interestingly, the nitrogen distribution feature detected here is different from the conventional core/shell structure reported in the nitrided Ti and Fe NPs^{14,15}, implying a distinct nitrogen diffusion process and special attention to the twin boundary in the current FeNi NPs.

Figure 3e shows the annular bright-field scanning transmission electron microscopy (ABF-STEM) image of the FeNi NP marked as “C” in Fig. 3a. The multiple bright/dark stripe diffraction contrasts in the ABF-STEM image, which is due to the lattice direction change across the twin boundaries (TBs), reveals a high-density nanotwin substructure in the nitrided FeNi NPs. The low-magnification TKD grain boundary maps (refined rotation angle: 55–65°, shown in Supplementary **Fig. S1**) reveal that nearly 49.5% of the as ITP processed and ~38.1% of the nitrided FeNi NPs contained nanotwin substructure. Such intensive nanotwins in the FeNi NPs may have formed during the quenching of the ITP process (quenching twins or mechanical twins¹⁶), induced by the thermal strain energy field relief or nitridation process (annealing twins¹⁷), a consequence of the recrystallisation/phase transformation of face-centred cubic (fcc) metals

with low stacking fault energies. Surprisingly, we observe significant solutes segregation at the TBs detected in the corresponding EDS maps (Fig. 3f-i). The line scan profiles across the nanotwinned regions (Fig. 3j) indicate a clear enrichment of Fe, and N while depletion of Ni occurs at the TBs (indicated by the arrows in Fig. 3j). More solutes segregation examples (EDS maps) can be found in Supplementary **Fig. S2**. To confirm whether such solutes segregation initially occurs during the thermal plasma process or the nitridation process, EDS mapping was also checked for the as ITP processed FeNi NPs. Figure 3k-n shows the representative ABF-STEM images and corresponding EDS maps of the as ITP processed FeNi NPs. Although the typical nanotwins were observed in Fig. 3k, there was no visible solute segregation in the corresponding EDS maps (Fig. 3l-n) (see additional example in Supplementary **Fig. S3**), which indicates that solute segregation mostly arised during the nitridation process. Grain boundary segregation and solute diffusional phenomena are well reported interface characteristics^{18,19}. In contrast, coherent TBs are dislocation-free and have perfectly aligned atomic stacks, resulting in low interfacial energies compared to grain boundaries; thus, strong solute segregation is not initially expected at coherent TBs. However, several recent reports on different alloy systems have shown solute segregation along TBs and proved it is associated to the migrating heterophase interface boundary, driven by minimizing the intrinsic stacking fault, elastic strain, and/or total energy in the system²⁰⁻²². On the other hand, it is also worth notice that solutes accumulation at the TBs can also act as Cottrell clouds surrounding the twins and thereby restrict further slip of the dislocations which was well discussed as the strength enhancement mechanism for the twinned soft materials²³⁻²⁵. Since the strong twin boundary-dislocation pinning interaction, the twin growth and/or detwinning process which determined by the dislocation motion will become time dependent. It could be one of possible reasons why the synthesis of the FeNiN precursor phase is the most time-consuming part of the nitrogen topotactic reaction route.

Figure 4a,c presents the atomic-resolution angle annular dark-field (ADF)-STEM images viewed along the $[\bar{1}10]$ zone axis to elucidate the detailed features of the atomic stacking and TBs of the as ITP processed and nitrided FeNi NPs, respectively. From the ADF-STEM images, the stacking faults parallel to the $(11\bar{1})$ plane creates nanotwin substructures in the matrix with a width varying from 2 (~ 0.5 nm) to 16 atomic layers (~ 3.5 nm). The nanotwin substructures are also confirmed by the typical two-set patterns presented in the fast Fourier transform (FFT) images in Supplementary **Fig. S4**. For the as ITP processed A1-FeNi NP in Fig. 4a, the (110) interplanar spacing in the nanotwinned region (marked as “**B**” in Fig. 4a, $= 0.255$ nm) seems to expand slightly compared to the matrix region (marked as “**A**” in Fig. 4a, $= 0.253$ nm). More remarkable (110) interplanar spacing expansion is detected in the nitrided FeNi NP with $= 0.278$ nm in the nanotwinned region (marked as “**B**” in Fig. 4c), while $= 0.243$ nm in the nanotwinned region (marked as “**A**” in Fig. 4c). Furthermore, the (111) planes in both the matrix and nanotwinned regions, which are supposed to be related by mirror symmetry with respect to the $(11\bar{1})$ twining plane, possess relatively different tilted angles, as indicated in Fig. 4a (70.5 vs. 72.8°). The degradation in the mirror symmetry becomes more serious in the nitrided FeNi NPs, as indicated in Fig. 4c (66.2 vs. 76.5°) which finally result in an “incoherent” twin boundaries with much higher boundary energy than a coherent twin boundaries²⁶. To estimate the lattice distortion/strain distribution at the nanotwinned regions, a

geometric phase analysis (GPA) was conducted to reconstruct strain maps from the corresponding atomic-resolution ADF-STEM images (see **Methods**). **Figure 4b,d** shows the shear strain (ϵ_{xy}) field maps of the as ITP processed and nitrided FeNi NPs, respectively. Although the atomic strain analysis is affected by camera resolution, the difference in the shear strain maps is substantial, indicating the qualitative difference in the lattice distortion between the twin and matrix regions of both the as ITP processed and nitrided FeNi NPs. The bright contrast in the shear strain maps which indicating positive shear strain suggests that the crystal units are significantly stretched along the [110] direction (which is close to xy direction) and compressed in the [002] direction for both the as ITP processed and nitrided FeNi NPs. Furthermore, a comparison of the interplanar spacing of the (110) and (002) planes between the matrix and nanotwinned regions of the nitride FeNi NPs (spacing calculated from Fig. 4c) reveals a +12.8% expansion along the [110] direction and -10.2% shrinkage along the [002] direction in the nanotwinned region (the bright region in Fig. 4d). The severe shear strain triggers the dislocation accumulations in the nanotwinned region, which eventually lead to significant lattice distortions as well as the detected (111) plane expansion. Similar phenomena has been reported by Wu *et al.* in the FeCoCrNi high-entropy alloy²⁷.

Thus, we have experimentally demonstrated that: a) twins are typical features present in both the as ITP processed (~49%) and nitrided FeNi NPs (~38%); b) in some of the nanotwinned regions, there is a visible enrichment of Fe and N solutes while a depletion of Ni at the TBs; c) the nanotwinned region suffers from severe shear strain ($\epsilon_{xy} \sim 10\%$) which consequently induces a significant lattice distortion as well as a lattice expansion. The expanded lattice planes in the nanotwinned region will open a channel and favours the diffusion of nitrogen atoms into the core of the FeNi NPs; meanwhile, the enriched Fe at the TBs can attract more nitrogen due to its relatively smaller iron-nitride formation energy than nickel-nitride²⁸. Thus, it is believed that such nanotwinned regions with relatively higher nitrogen concentration and low-symmetry crystal will be energy favourable to promote the nucleation of the FeNiN precursor phase.

Massive transformation of Fe₂Ni₂N to FeNiN phase. As mentioned previously, the FeNiN product phase possesses different nitrogen concentrations and crystal structures compared to the Fe₂Ni₂N parent phase; thus, one can detect sharp and sometimes straight phase boundaries in nitrided FeNi NPs (as illustrated in Fig. 3b,d) in which the phase transformation is not fully complete. Therefore, after the preferential nucleation of the FeNiN product phase in the nanotwinned region, it is important to understand how this new product phase grow into the Fe₂Ni₂N parent matrix. To clarify this critical question, a detailed microstructure analysis focusing on the FeNiN/Fe₂Ni₂N phase boundaries was performed.

Figure 5a,b,c shows the ABF-STEM images of the nitrided FeNi NPs in which the distinct bright/dark phase contrast indicates clear FeNiN/Fe₂Ni₂N phase boundaries. **Figure 5d,e,f** shows the corresponding EDS composite (Fe (red)-Ni (blue)-N (green)) maps. The light yellow/pink contrast illustrates a relatively N-rich/-poor zone, which was later identified corresponding to the FeNiN product/Fe₂Ni₂N matrix phase by matching the lattice spacing and indexing in the FFT patterns and the atomic-resolution ADF-STEM

image (see Supplementary **Fig. S5**). The clear, sharp, and sometimes straight phase boundaries are consistent with the phase/elements distribution characteristics observed in Fig. 3b,d. With detailed microstructure characterisation (Fig. 5g,h,i) of the FeNiN/Fe₂Ni₂N phase boundaries, it is surprising that the FeNiN product phase usually develops a high-index/irrational orientation relationship (OR) with the Fe₂Ni₂N parent matrix. The FeNiN/Fe₂Ni₂N phase boundary displayed in Fig. 5g (corresponding to the dash squared region in Fig. 5d) seems to show a high-index/irrational OR at the interface with the Fe₂Ni₂N phase on a [110] zone axis, while the FeNiN phase is tilted slightly away from the exact zone axes. In Fig. 5h (corresponding to the dash squared region in Fig. 5e), the FeNiN/Fe₂Ni₂N phase boundary demonstrates a sharp/fully epitaxial coherent interface with the Fe₂Ni₂N phase on a [100] zone axis, while the FeNiN phase is tilted slightly away from the exact zone axes. Finally, in Fig. 5i (corresponding to the dash squared region in Fig. 5f), the FeNiN/Fe₂Ni₂N phase boundary demonstrates an atomic rough incoherent interface with the FeNiN phase on a [113] zone axis, while the Fe₂Ni₂N phase is tilted slightly away from the [001] zone axes. The possible high-index OR developed at the FeNiN/Fe₂Ni₂N interface is illustrated in Fig. 5j: $(12\bar{1})_{\text{FeNiN}} \parallel [113]_{\text{FeNiN}} \parallel (100)_{\text{Fe}_2\text{Ni}_2\text{N}} \parallel [001]_{\text{Fe}_2\text{Ni}_2\text{N}}$. Such a high-index OR results in a small lattice misfit (1.8%) at the interface which favours a lower strain/interfacial energy. The results indicate that it is possible for two phases with a high-index OR, and to obtain some degree of atomic matching across the high-index interface planes by selecting a suitable interface plane in the nitrided FeNi NPs. However, some occasional planes apparently have no matching planes on the opposing side of the boundary, makes such an interface partly coherent in the plane-to-plane geometry. The absence of a lattice correspondence defines such a FeNiN/Fe₂Ni₂N interface in Fig. 5i as structurally incoherent. Thus, the FeNiN/Fe₂Ni₂N phase boundaries in the nitrided FeNi NPs present both a structurally commensurate (coherent) and incommensurate (incoherent) interface, with a variable degree of commensurability depending on the orientation and planarity of a particular interface.

Figure 5k,l shows the relative low-magnification ABF-STEM images of the FeNiN/Fe₂Ni₂N interfaces displayed in Fig. 5a and 5c, respectively. It demonstrates the typical terraces/ledges featured at the interfaces, implying that the growth of the FeNiN product phase, accompanied by the prorogation of the interfaces, follows a ledge mechanism^{29,30}. This kind of ledgewise growth motion of the interface has been reported in the FeNi^{31,32}, MnAl^{21,33}, and TiAl^{34,35} alloy systems associated with the massive transformation process. It has been experimentally demonstrated that massive transformations involve a special crystallographic OR between the parent and the product phases, leading to coherent nucleation. This is followed by growth, in which the interface changes from coherent to partly coherent, or even to a high-index irrational interface, and migrates by a ledge mechanism^{29,30}, which is principally accomplished by short-range atom jumps that occur almost continuously across the structurally incoherent interfaces^{21,34}. The massive γ to α transformation was previously reported in the FeNi binary alloy system (with a Ni concentration $\leq 15\%$)³⁶⁻³⁸. The present results of elements segregated at the TBs (Fig. 3i,j), the high-index OR developed at the FeNiN/Fe₂Ni₂N interface (Fig. 5g-j), and the ledgewise growth motion of the FeNiN/Fe₂Ni₂N interface (Fig. 5k,l) agrees well with the typical characteristics of a

massive transformation, indicating that the FeNiN phase is most likely formed through a massive transformation from the $\text{Fe}_2\text{Ni}_2\text{N}$ matrix phase during the nitridation process. And this is the first experimental demonstration of a massive transformation in the Fe-Ni-N system. Based on our experimental results, one possible formation route for the FeNiN precursor phase during the nitridation process is proposed as follows: First, the FeNiN product phase initially energetically favours to nucleation at the nanotwinned region in the $\text{Fe}_2\text{Ni}_2\text{N}$ parent matrix. Then the FeNiN/ $\text{Fe}_2\text{Ni}_2\text{N}$ interface develops a high-index OR through the short-range atoms jump across the interface to minimise the strain/interface energy. Finally, the massive $\text{Fe}_2\text{Ni}_2\text{N}$ to FeNiN phase transformation is accomplished through the migration of the high-index OR interfaces following a ledge mechanism. In some nanotwinned regions, solutes segregation at the TBs during the massive transformation may occur and block the dislocation motion which will restrict the FeNiN/ $\text{Fe}_2\text{Ni}_2\text{N}$ interface migration and finally leads to a time-consuming phase transformation process.

Conclusion

In this work, we investigated the formation mechanism of the FeNiN phase (the precursor phase of the L1_0 -ordered FeNi for synthesise of rare-earth-free permanent magnets) in FeNi NPs during nitridation process. We found that the intensive nanotwins in the nitrified FeNi NPs possess a distorted lattice and relatively higher nitrogen concentration, which could provide preferential nucleation sites for the FeNiN product phase in the FeNi_2N_2 parent matrix. Furthermore, detailed microstructure analysis revealed that the growth of the FeNiN product phase followed a massive transformation with high-index irrational orientation relationships and ledgewise growth motion characteristics detected at the FeNiN/ $\text{Fe}_2\text{Ni}_2\text{N}$ migrating interface. Based on the results, we delineated a potential formation route of the FeNiN precursor phase in the FeNi NPs during nitridation, which could contribute to the basic understanding of this mechanism and promote further optimisation of the synthesis of bulk ordered FeNi alloys for various magnetic applications.

Methods

Materials synthesis. FeNi nanoparticles (NPs) were synthesised using a low oxygen induction thermal plasma (LO-ITP) system (TP-40020NPS, JEOL Co., Ltd.) and a powder feeding system (TP-99010FDR, JEOL). The detailed configuration information of the LO-ITP system can be found in Ref.³⁹. Fe ($D = 3-5 \mu\text{m}$, 99.9% purity) and Ni ($D = 3-5 \mu\text{m}$, 99.9% purity, Kojundo Chemical Lab. Co., Ltd., Japan) powders were used as starting materials and mixed with a mole ratio of Fe:Ni = 1:1. The ITP was generated using a radio frequency generator with a power of 6 kW and a frequency of 13.56 MHz. G1 grade Ar gas (oxygen level of less than 0.1 ppm) was used as the plasma gas with a flow rate of 35 L/min and as a powder feeding gas with a flow rate of 3 L/min using a powder feeding system (TP-99010FDR, JEOL Ltd.). The mixed powders were continuously introduced from the top of the thermal plasma using a powder feeder for 10 min. After the ITP process, the processed NPs were collected from the water-cooled chamber wall and handled in a glovebox with an oxygen level below 0.5 ppm.

The as ITP processed FeNi NPs were first reduced in an electric furnace at 400 °C under a hydrogen gas flow at 1 L/min for 2 h. Then, the processed NPs were nitrided at 350 °C under a large amount of ammonia gas flowing at a rate of 2 L/min for 16 h. To prevent oxidation, most of the experiments and evaluations in this work were carried out under a low oxygen atmosphere (glovebox) without exposure to the atmosphere, except when briefly removing the samples for characterisation by SEM and transmission electron microscopy (TEM).

Theoretical calculation. The energies of the randomly disordered and $L1_0$ -ordered FeNi alloys and their nitrides were calculated using the spin-polarised density functional theory formalism^{40,41}. Ultrasoft-type pseudopotentials with a plane wave basis set were used to describe the electronic structure within the generalized-gradient approximation (GGA) using the parameters by Perdew, Burke, and Ernzerhof (PBE)⁴². The computations were carried out using the PWscf code implemented in the QUANTUM ESPRESSO package^{43,44}. The k -points for the Brillouin zone integration were sampled on a $4 \times 4 \times 4$ grid according to the Monkhorst-Pack scheme⁴⁵. The kinetic energy cut-offs for the wavefunctions and charge density were 90 Ry and 1080 Ry, respectively. The self-consistent field convergence was determined by the threshold value of 10^{-6} Ry for the estimated energy error.

A $2 \times 2 \times 2$ supercell (32 metal atoms) of the FeNi fcc or tetragonal (fct) unit cells (four metal atoms) was used to express the random alloy state. Repeat random assignments of each half of the 32 transition element sites to Fe and Ni was achieved using computer-generated pseudorandom numbers. One FeNi arrangement was unbiasedly selected from those with an order parameter of $S = 0$ and was used in the calculation of the random states. For structural relaxation, we did not perform a full optimisation for each individual atom, but only optimised the lattice constants. The relative positions of the metal atoms within the unit cell were fixed at the ideal position of the fcc or fct lattice. The energies of each state were defined as the formation energies from the lowest energy polytypes of the constituent elements, namely bcc-Fe, fcc-Ni, and an isolated N_2 molecule.

Structural characterization. The phases were identified using an X-ray diffractometer (PANalytical, Empyrean, Co- $K\alpha$, $\lambda = 1.78901 \text{ \AA}$). The particle morphology and size distribution were estimated from images captured using a field-emission scanning electron microscope (FE-SEM, JSM-7800F, JEOL).

Nanoscale crystallographic/phase characterisation was performed using TKD analysis. TKD (also known as transmission electron backscatter diffraction (t-EBSD)) is an electron diffraction method used in SEM that offers a dramatic improvement in spatial resolution ($2\text{--}5 \text{ nm}^{46}$) over traditional EBSD, which is comparable to nano-diffraction techniques in TEM⁴⁷. The epoxy-embedded FeNi NPs were first sliced (cross-section sample) and fixed on a Cu grid via an FEI Scios focused ion beam–scanning electron microscopy (FIB-SEM) facility. A conventional EBSD detector (EDAX DigiView 5 with EDAX TEAM software) was used for the TKD analysis. TSL-OIM 7 software was used to post-process the TKD raw data.

The high-resolution scanning transmission electron microscopy (STEM), EELS, and EDS mapping were carried out on identical Cu grid specimens by employing an atomic-resolution analytical electron microscope JEM-ARM200F (JEOL Ltd. Tokyo, Japan). The system includes an imaging Cs corrector and is operated at an acceleration voltage of 200 kV.

The magnetic properties were measured using a physical property measurement system equipped with a vibrating sample magnetometer (PPMS-VSM/Quantum Design, Dynacool). The maximum field for the measurement was 90 kOe.

Strain mapping. The strain distribution around the nanotwinned regions of FeNi NPs was analysed using a geometric phase analysis (GPA)⁴⁸ on the individual atomic-resolution HAADF-STEM images. GPA is normally used to measure in-plane displacements and/or strains at the nanometre scale within an atomic-resolution TEM field of view using a FFT-based analysis of the local lattice parameters^{48,49}. Before GPA, over 20 aberration-corrected STEM images were acquired from the same region and the corresponding atomic positions were averaged/shift corrected to minimise the possible influence of vibration during scanning on the strain maps. Then, with the two-dimensional atomic arrangement shown in the STEM images, the tensorial distortion is defined as⁴⁸

$$e = \begin{pmatrix} e_{xx} & e_{xy} \\ e_{yx} & e_{yy} \end{pmatrix} = \begin{pmatrix} \partial u_x / \partial x & \partial u_x / \partial y \\ \partial u_y / \partial x & \partial u_y / \partial y \end{pmatrix} \quad (1)$$

where $\mathbf{u} = (u_x, u_y)$ denotes the displacement field. In addition, the shear strain in this study is defined as:

$$\varepsilon_{xy} = \varepsilon_{yx} = 1/2 \left(\partial u_x / \partial y + \partial u_y / \partial x \right) \quad (2)$$

The GPA in this work was conducted with an open-source software Strain++⁴⁹.

Declarations

Acknowledgments

The authors thank A. Hosokawa for valuable discussions and K. Hayakawa for technical supports. This work was partially supported by the Future Pioneering Program project “Development of Magnetic Material Technology for High-Efficiency Motors” commissioned by Japan’s New Energy and Industrial Technology Development Organization (NEDO).

Author contributions

Y.H. and J.W. conceived the project. K.O. and K.T administrative supervise this research project. Y.H. and K.P. fabricated the samples. K.S performed the nitridation process. J.W. and K.P. carried out the measurements (XRD and SEM). Z.L. and J.W. conducted the observations and structural analysis using TEM. J.W. carried out the data analysis (strain mapping and crystallography). W.Y. supported the model building and theoretical calculations. J.W. and H.Y. wrote the manuscript. All the authors contributed to the discussion of the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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References

1. Hugon, C., D'Amico, F., Aubert, G. & Sakellariou, D. Design of arbitrarily homogeneous permanent magnet systems for NMR and MRI: Theory and experimental developments of a simple portable magnet. *J Magn Reson*, **205**, 75–85 <https://doi.org/doi:10.1016/j.jmr.2010.04.003> (2010).
2. Coey, J. M. D. Permanent magnet applications. *Journal of Magnetism and Magnetic Materials* **248**, 441–456, doi:Pii S0304-8853(02)00335-9Doi 10.1016/S0304-8853(02)00335-9 (2002)
3. Liang, T., Li, K. X. & Wang, L. Q. State of rare earth elements in different environmental components in mining areas of China. *Environ Monit Assess*, **186**, 1499–1513 <https://doi.org/doi:10.1007/s10661-013-3469-8> (2014).
4. Goodenough, K. M., Wall, F. & Merriman, D. The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations. *Nat Resour Res*, **27**, 201–216 <https://doi.org/doi:10.1007/s11053-017-9336-5> (2018).
5. Cui, J. *et al.* Current progress and future challenges in rare-earth-free permanent magnets. *Acta Mater*, **158**, 118–137 <https://doi.org/doi:10.1016/j.actamat.2018.07.049> (2018).
6. Neel, L., Dautreppe, D., Laugier, J., Pauleve, J. & Pauthenet, R. Magnetic Properties of Iron-Nickel Single Crystal Ordered by Neutron Bombardment. *J Appl Phys*, **35**, 873– <https://doi.org/doi:10.1063/1.1713516> (1964).
7. Pauleve, J., Krebs, C. A., Bourret, A. & K. & Magnetization Curves of Fe-Ni (50-50) Single Crystals Ordered by Neutron Irradiation with an Applied Magnetic Field. *J Appl Phys*, **39**, 989– <https://doi.org/doi:10.1063/1.1656361> (1968).
8. Lee, S. *et al.* Formation of FeNi with L1(0)-ordered structure using high-pressure torsion. *Phil Mag Lett*, **94**, 639–646 <https://doi.org/doi:10.1080/09500839.2014.955546> (2014).
9. Makino, A. *et al.* Artificially produced rare-earth free cosmic magnet. *Sci Rep*, **5**, 16627 <https://doi.org/doi:10.1038/srep16627> (2015).

10. Shima, T., Okamura, M., Mitani, S. & Takanashi, K. Structure and magnetic properties for L1(0)-ordered FeNi films prepared by alternate monatomic layer deposition. *Journal of Magnetism and Magnetic Materials*, **310**, 2213–2214 <https://doi.org/doi:10.1016/j.jmmm.2006.10.799> (2007).
11. Takanashi, K., Mizuguchi, M., Kojima, T. & Tashiro, T. Fabrication and characterization of L1(0)-ordered FeNi thin films. *J Phys D Appl Phys* **50**, doi:ARTN 48300210.1088/1361-6463/aa8ff6 (2017)
12. Goto, S. *et al.* Synthesis of single-phase L1₀-FeNi magnet powder by nitrogen insertion and topotactic extraction. *Sci Rep*, **7**, 13216 <https://doi.org/doi:10.1038/s41598-017-13562-2> (2017).
13. Izumi, F. & Momma, K. Three-dimensional visualization in powder diffraction. *Solid State Phenomena*, **130**, 15–20 <https://doi.org/doi:DOI 10.4028/www.scientific.net/SSP.130.15> (2007).
14. Zhang, Y. S. *et al.* Core-shell structured titanium-nitrogen alloys with high strength, high thermal stability and good plasticity. *Sci Rep-Uk* **7**, doi:ARTN 4003910.1038/srep40039(2017)
15. Ma, B., Liu, J. M., Guo, G. N. & Wang, J. P. Critical thickness of alpha "-Fe16N2 layer prepared in low-temperature nitriding. *J Appl Phys* **128**, doi:ArtN 22390210.1063/5.0033577 (2020)
16. Cheng, W. C., Lin, Y. S. & Chen, K. F. The formation of ferrite quenching twins in a body-centered cubic Fe-Mn-Al alloy during high-temperature quenching. *Scripta Mater*, **81**, 36–39 <https://doi.org/doi:10.1016/j.scriptamat.2014.02.021> (2014).
17. Roy, B. & Das, J. Strengthening face centered cubic crystals by annealing induced nanotwins. *Sci Rep-Uk* **7**, doi:ARTN 1751210.1038/s41598-017-17848-3 (2017)
18. Wang, Z. C. *et al.* Atom-resolved imaging of ordered defect superstructures at individual grain boundaries., **479**, 380–383 <https://doi.org/doi:10.1038/nature10593> (2011).
19. Buban, J. P. *et al.* Grain boundary strengthening in alumina by rare earth impurities., **311**, 212–215 <https://doi.org/doi:10.1126/science.1119839> (2006).
20. He, C., Li, Z., Chen, H., Wilson, N. & Nie, J. F. Unusual solute segregation phenomenon in coherent twin boundaries. *Nat Commun*, **12**, 722 <https://doi.org/doi:10.1038/s41467-021-21104-8> (2021).
21. Palanisamy, D., Raabe, D. & Gault, B. On the compositional partitioning during phase transformation in a binary ferromagnetic MnAl alloy. *Acta Mater*, **174**, 227–236 <https://doi.org/doi:10.1016/j.actamat.2019.05.037> (2019).
22. Nie, J. F., Zhu, Y. M., Liu, J. Z. & Fang, X. Y. Periodic Segregation of Solute Atoms in Fully Coherent Twin Boundaries., **340**, 957–960 <https://doi.org/doi:10.1126/science.1229369> (2013).
23. Kim, J. G. *et al.* Superior Strength and Multiple Strengthening Mechanisms in Nanocrystalline TWIP Steel. *Sci Rep-Uk* **8**, doi:ARTN 1120010.1038/s41598-018-29632-y(2018)
24. Ghazisaeidi, M., Hector, L. G. & Curtin, W. A. Solute strengthening of twinning dislocations in Mg alloys. *Acta Mater*, **80**, 278–287 <https://doi.org/doi:10.1016/j.actamat.2014.07.045> (2014).
25. Lu, L., Shen, Y. F., Chen, X. H., Qian, L. H. & Lu, K. Ultrahigh strength and high electrical conductivity in copper., **304**, 422–426 <https://doi.org/doi:DOI 10.1126/science.1092905> (2004).
26. Porter, D. A. *Phase transformations in metals and alloys*. 4th edition. edn, (CRC Press, 2022)

27. Wu, W. Q. *et al.* Dual mechanisms of grain refinement in a FeCoCrNi high-entropy alloy processed by high-pressure torsion. *Sci Rep-Uk* 7, doi:ARTN 4672010.1038/srep46720(2017)
28. Imai, Y., Sohma, M. & Suemasu, T. Energetic stability and magnetic moment of tri-, tetra-, and octa-ferromagnetic element nitrides predicted by first-principle calculations. *Journal of Alloys and Compounds*, **611**, 440–445 <https://doi.org/doi:10.1016/j.jallcom.2014.04.171> (2014).
29. Aaronson, H. I., Laird, C. & Kinsman, K. R. Application of a Theory of Precipitate Morphology to Massive Transformation. *Scripta Metall Mater*, **2**, 259–, doi:[https://doi.org/Doi 10.1016/0036-9748\(68\)90117-8](https://doi.org/Doi 10.1016/0036-9748(68)90117-8) (1968).
30. Menon, E. S. K., Plichta, M. R. & Aaronson, H. I. Some Aspects of the Massive Transformation. *Acta Metall Mater*, **36**, 321–332 [https://doi.org/doi:Doi 10.1016/0001-6160\(88\)90009-0](https://doi.org/doi:Doi 10.1016/0001-6160(88)90009-0) (1988).
31. Wu, J., Howe, J. M. & Zhang, W. Z. An in situ transmission electron microscopy study of interface growth during martensitic transformation in an Fe-Ni-Mn alloy. *Acta Mater*, **59**, 3297–3303 <https://doi.org/doi:10.1016/j.actamat.2011.02.003> (2011).
32. Momprou, F., Wu, J. & Zhang, W. Z. A preliminary in-situ TEM study of martensite/austenite interface migration in an Fe-20Ni-5.4Mn alloy. *Mater Today-Proc*, **2**, 651–654 <https://doi.org/doi:10.1016/j.matpr.2015.07.368> (2015).
33. Yanar, C., Wiezorek, J. M. K., Radmilovic, V. & Soffa, W. A. Massive transformation and the formation of the ferromagnetic L1(0) phase in manganese-aluminum-based alloys. *Metall Mater Trans A*, **33**, 2413–2423 <https://doi.org/doi:DOI 10.1007/s11661-002-0363-3> (2002).
34. Howe, J. M., Reynolds, W. T. & Vasudevan, V. K. Static and in-situ high-resolution transmission electron microscopy investigations of the atomic structure and dynamics of massive transformation interfaces in a Ti-Al alloy. *Metall Mater Trans A*, **33**, 2391–2411 <https://doi.org/doi:DOI 10.1007/s11661-002-0362-4> (2002).
35. Veeraraghavan, D., Wang, P. & Vasudevan, V. K. Nucleation kinetics of the $\alpha \rightarrow \gamma(M)$ massive transformation in a Ti-47.5 at.% Al alloy. *Acta Mater*, **51**, 1721–1741 [https://doi.org/doi:10.1016/S1359-6454\(02\)00572-4](https://doi.org/doi:10.1016/S1359-6454(02)00572-4) (2003).
36. Zhu, J. N. *et al.* Determination of the intrinsic α/γ interface mobility during massive transformations in interstitial free Fe-X alloys. *Acta Mater*, **133**, 258–268 <https://doi.org/doi:10.1016/j.actamat.2017.05.045> (2017).
37. Borgenstam, A. & Hillert, M. Massive transformation in the Fe-Ni system. *Acta Mater*, **48**, 2765–2775 [https://doi.org/doi:Doi 10.1016/S1359-6454\(00\)00102-6](https://doi.org/doi:Doi 10.1016/S1359-6454(00)00102-6) (2000).
38. Gilbert, A. & Owen, W. S. Diffusionless Transformation in Iron-Nickel, Iron-Chromium and Iron-Silicon Alloys. *Acta Metall Mater*, **10**, 45–, doi:[https://doi.org/Doi 10.1016/0001-6160\(62\)90185-2](https://doi.org/Doi 10.1016/0001-6160(62)90185-2) (1962).
39. Hirayama, Y., Suzuki, K., Yamaguchi, W. & Takagi, K. Cold welding behavior of fine bare aluminum powders prepared by new low oxygen induction thermal plasma system. *Journal of Alloys and Compounds*, **768**, 608–612 <https://doi.org/doi:10.1016/j.jallcom.2018.07.275> (2018).
40. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys Rev*, **140**, 1133– <https://doi.org/doi:DOI 10.1103/PhysRev.140.A1133> (1965).

41. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Phys Rev B*, **136**, B864–+ <https://doi.org/doi:DOI 10.1103/PhysRev.136.B864> (1964).
42. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys Rev Lett*, **77**, 3865–3868 <https://doi.org/doi:DOI 10.1103/PhysRevLett.77.3865> (1996).
43. Giannozzi, P. *et al.* Advanced capabilities for materials modelling with QUANTUM ESPRESSO. *J Phys-Condens Mat* **29**, doi:ARTN 46590110.1088/1361-648X/aa8f79(2017)
44. Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J Phys-Condens Mat* **21**, doi:Artn 39550210.1088/0953-8984/21/39/395502(2009)
45. Pack, J. D. & Monkhorst, H. J. Special Points for Brillouin-Zone Integrations - Reply. *Phys Rev B*, **16**, 1748–1749 <https://doi.org/doi:DOI 10.1103/PhysRevB.16.1748> (1977).
46. Trimby, P. W. Orientation mapping of nanostructured materials using transmission Kikuchi diffraction in the scanning electron microscope., **120**, 16–24 <https://doi.org/doi:10.1016/j.ultramic.2012.06.004> (2012).
47. Trimby, P. W. *et al.* Characterizing deformed ultrafine-grained and nanocrystalline materials using transmission Kikuchi diffraction in a scanning electron microscope. *Acta Mater*, **62**, 69–80 <https://doi.org/doi:10.1016/j.actamat.2013.09.026> (2014).
48. Hytch, M. J., Snoeck, E. & Kilaas, R. Quantitative measurement of displacement and strain fields from HREM micrographs., **74**, 131–146 [https://doi.org/doi:Doi 10.1016/S0304-3991\(98\)00035-7](https://doi.org/doi:Doi 10.1016/S0304-3991(98)00035-7) (1998).
49. Peters, J. J. P. *et al.* Artefacts in geometric phase analysis of compound materials., **157**, 91–97 <https://doi.org/doi:10.1016/j.ultramic.2015.05.020> (2015).

Figures

Figure 1

Energy diagram between the related states of the FeNi alloys during the nitriding/denitriding process. The random disordered FeNiN phase has a much higher energy than that of the L10-ordered phase.

Temporary and local over-nitriding of Fe₂Ni₂N may promote rearrangement of the metal elements. Red, blue, and green spheres denote iron, nickel, and nitrogen atoms, respectively.

Figure 2

Microstructure evolution before and after the nitriding process. (a, b) FE-SEM images and (c) XRD profiles of the (a, c-i) as induction thermal plasma processed and (b, c-ii) nitrided FeNi NPs. Insets in the FE-ESEM images show the corresponding particle size distribution.

Figure 3

Correlation between FeNiN phase and nanotwins. (a) TKD image quality (IQ) map and (b) TKD phase map of the nitrided FeNi NPs. The interfaces between the FeNiN (in red) product and Fe₂Ni₂N (in green) parent phases are indicated with the white arrow in the phase map (b). EELS elemental maps of (c) Fe and (d) N of nitrided FeNi NPs marked as “B” in the IQ map (a). Angular bright-field STEM images (e, k) and EDS elemental maps (f-i and l-n) of the (e-i) nitrided and (k-n) as induction thermal plasma processed FeNi NPs. (j) A line elements scan profile of the nitrided FeNi NP across the nanotwinned region as the line marked in the composite map (i).

Figure 4

Shear stress induced lattice distortion and incoherence at the nanotwinned region. (a, c) High-resolution HAADF-STEM images demonstrating parallel multi-nanotwin TBs along the (111($\bar{}$)) plane are indicated by the dashed lines) and (b, d) corresponding GPA strain maps showing the shear strain (strain tensor component ϵ_{xy}) of the (a, b) as induction thermal plasma processed and (c, d) nitrided FeNi NPs. The colour scale bar for strain ranges from -10% (dark blue) to +10% (white).

Figure 5

Coherent/incoherent Fe₂Ni₂N/FeNiN phase interfaces with ledgewise growth features. (a-c) ABF-STEM images and (d-f) the corresponding combined (Fe, Ni, and N) elements distribution mapping of the nitrated FeNi NPs. (g-i) High-resolution ABF-STEM images focusing on the detailed microstructure of the FeNiN/Fe₂Ni₂N interfaces. The observed areas are indicated by the dashed squares marked in the corresponding element distribution maps (d-f). The high-index/irrational OR developed at the

FeNiN/Fe₂Ni₂N coherent (h)/incoherent (g and i) interfaces were indicated by the dashed line and one representative high-index orientation relationship present in (i) is schematised in (j). (k,l) ABF-STEM images of nitrided FeNi NPs with terraces/ledges demonstrating the ledgewise growth motion of the FeNiN/Fe₂Ni₂N phase interface in (a) and (c), respectively.

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