Precipitate transformation from NiAl-type to Ni₂AlMn-type and its influence on the mechanical properties of high-strength steels

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Abstract

The precipitate transformation from NiAl-type to Ni₂AlMn-type and its influence on the mechanical properties of the Fe-5Ni-1Al-xMn ($x = 0, 1, 3$, and 5 wt.%) alloys were studied thoroughly through a combination of three-dimensional atom probe tomography (APT), first-principles calculations and mechanical tests. APT reveals the precipitation of NiAl-type nanoparticles in the 0-3Mn alloys and the co-precipitation of fine NiAl-type and coarse Ni₂AlMn-type nanoparticles in the 5Mn alloy, in which the Ni₂AlMn-type nanoparticles are formed as a result of the coarsening of the NiAl-type ones. The first-principles calculations indicate that the Ni₂AlMn-type nanoparticles are energetically more favorable than the NiAl-type ones, but their nucleation and growth kinetics are relatively slow, resulting in the initial precipitation of the NiAl-type nanoparticles and the later precipitate transformation from NiAl-

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type to Ni₂AlMn-type. A quantitative analysis of the strengthening mechanism reveals that although the Ni₂AlMn-type nanoparticles have a higher strengthening efficiency than the NiAl-type ones, they make a minor contribution to the total strengthening effects due mainly to their small number density. In addition, the Ni₂AlMn-type nanoparticles with a composition consistent with that of the Heusler phase are likely to~~hard and brittle Ni₂AlMn-type Heusler nanoparticles~~ promote the brittle cleavage and intergranular fracture of the 5Mn alloy, resulting in a significant decrease of the alloy ductility.

Keywords: precipitation; phase transformation; precipitation strengthening; atom probe tomography; mechanical property

1. Introduction

High-strength steels offer a high potential for both considerable improvements in performance and reduction in weight for many lightweight applications, such as aerospace, wind energy, vehicles and shipbuilding. Basically, the strengthening of crystalline materials involves the controlled creation of internal obstacles to impede the motion of dislocations [1]. Uniform precipitation of nanoparticles has been recognized as one of the most effective methods of strengthening low-carbon steels [~~2-11~~2-12], which allows the development of advanced steels with a good combination of high strength, high ductility and good weldability. The magnitude of the strengthening so obtained is highly dependent upon the microstructure and micro-mechanical properties of the nanoparticles, which in turn is determined by their composition and crystal structure [1]. Fundamentally, the chemical and crystal nature of the nanoparticles in steels is influenced by the thermodynamic properties, such as the elastic and interfacial energies, as well as the chemical driving force for precipitation, and the kinetics of the system, such as the activation barrier for nucleation and diffusion of the different species [~~12~~13]. In multi-component steels, more than one type of nanoparticles can be presented simultaneously or successively, depending on the alloy compositions and heat treatments [~~7-9~~7-10]. In addition, even for a specific type of nanoparticles, such as Cu-rich nanoparticles, their crystal structure and composition may undergo complex changes with aging time [~~13-15~~8,14-20]. Therefore, for an understanding and eventually control over the complex precipitation behavior of nanoparticle-strengthened steels, it is of fundamental importance to elucidate the precipitation mechanism, structural transition and compositional evolution of the nanoparticles.

Recently, a class of Fe-Ni-Al-Mn-based steels strengthened by high number densities of Ni/Al/Mn-rich nanoparticles has received considerable attention due to their good combination of high strength, high ductility and relatively low cost [~~16-19~~21-24]. Previous studies indicate that this class of steels presents an interesting but complex precipitation behavior, which is highly sensitive to the alloy composition, especially the Mn content. For example, in low-Mn steels with less than 5 wt.% Mn, a small amount of Mn partitions to the NiAl-type nanoparticles by occupying the Al sublattice, leading to the formation of the B2-type Ni(Al,Mn) nanoparticles [8,9,20-22,25]. Given the smaller atomic radius of Mn compared with that of Al, Mn substitution would result in a better lattice mismatch with the bcc Fe matrix and hence a smaller nucleation barrier for the formation of NiAl-type nanoparticles, which dramatically increases the particle number density and enhances the precipitation strengthening response [~~16,17,20,21~~8,9,22]. In comparison, in medium- and high-Mn steels with more than 5 w.% Mn, the main strengthening agent has been found to be L2₁-type Ni₂AlMn Heusler nanoparticles, which is a further ordering of the B2 structure [~~22,23~~26,27]. It is found that the Ni(Al,Mn) nanoparticles with a fine dispersion are effective in strengthening steels without significantly compromising the ductility [21,22], whereas the Ni₂AlMn nanoparticles usually lead to an increase in strength but a loss in ductility, the degree of which depends strongly on the microstructure [27]. To date, however, the underlying mechanism of how the nanoparticles transform from NiAl-type to Ni₂AlMn-type is not clearly understood yet, and its influence on the mechanical properties of the Fe-Ni-Al-Mn-based steels remains elusive.

The purpose of this study is to elucidate the mechanism of the precipitate transformation from NiAl-type to Ni₂AlMn-type at the nanoscale, and further to understand how the precipitation transformation affects the strength and ductility of the Fe-5Ni-1Al-*x*Mn (*x* = 0, 1, 3,

and 5 wt.%) steels. The precipitation characteristics, including the size, number density, morphology, spatial distribution, composition, and solute partitioning behavior of the Ni-Al-enriched nanoparticles in the Fe-Ni-Al-Mn alloys with the different Mn contents were thoroughly investigated by atom probe tomography (APT), which is a unique powerful tool for the characterization of composition and nanostructural features of embedded nanoparticles with a near-atomic spatial resolution [2428]. Particular attention was paid to understanding the key factors governing the formation of the NiAl- and Ni₂AlMn-type nanoparticles and elucidating the correlation of the precipitation microstructure with the mechanical properties of these alloys.

2. Experimental

Four alloys with compositions of Fe-5Ni-1Al, Fe-5Ni-1Al-1Mn, Fe-5Ni-1Al-3Mn, and Fe-5Ni-1Al-5Mn (wt.%) were prepared by arc-melting a mixture of commercial-pure metals (purity >99.8 wt.%) in a Ti-gettered high-purity argon atmosphere. The alloy compositions are listed in both weight and atomic percent in Table 1. These alloys are hereafter referred to as 0Mn, 1Mn, 3Mn, and 5Mn alloys, respectively. The ingots were remelted five times to ensure chemical homogeneity. The melted alloys were then drop-cast into a copper mold with dimensions of 50 × 15 × 6 mm. The resulting plates were cold rolled by multiple passes with a total reduction of ~66% and solution-treated for 30 min. at 900 °C, followed by water quenching and then ageing isothermally at 550 °C for various time periods up to 486 h.

Hardness measurements were conducted in a Vickers hardness tester with a load of 2 N for 15 s, and for each specimen, at least 8 indents were measured to obtain an average value. Tensile samples with a cross-section of 3.2 × 1 mm and a gauge length of 12.5 mm were cut by electro-discharge machining, and ground careful on each side with SiC paper through 4000 grit. Tensile

tests along the rolling direction of the samples were conducted on an MTS tensile testing machine at a strain rate of 10^{-3} s^{-1} . Two specimens were tested in each condition, and the average values were reported. The yield strength was determined with the 0.2% offset plastic strain method. Fracture surfaces were examined by scanning electron microscopy (SEM).

The needle-shaped specimens for APT were fabricated by a combination of standard electropolishing methods followed by an annular mill in a FEI Nova 200 focused-ion beam/scanning electron microscope (FIB/SEM) [2529]. APT tips were electropolished using a solution of 2-10% perchloric acid (60%) in 2-butoxyethanol – performed in a Simplex Electropointer. With APT specimens in this automatic equipment, the current was allowed to vary continuously due to the needle-shaped specimen and the removal of material. The electropolishing to FIB point varied from specimen to specimen and the specimen material. It depended on end radius of the specimen which was controlled by the weight of the bottom half of the specimen at which the blank broke into two needle-shaped specimens. The first stages of milling were performed with a 30 keV Ga^+ ion beam and a current of 1-5 nA, and the final polishing was performed using a 2-5 keV Ga^+ ion beam and a current of 50-100 pA either in annual milling or broad beam mode. The APT characterizations were performed in a CAMECA Instruments LEAP 4000X HR local electrode atom probe. The specimen were analyzed in voltage mode with a specimen temperature of 50 K, a pulse repetition rate of 200 kHz, a pulse fraction of 0.2, and an ion collection rate of between 0.5% and 1% ions per field evaporation pulse. Imago Visualization and Analysis Software version 3.6.6 was used for three-dimensional reconstruction, composition analyses, and the creation of isoconcentration surfaces. The Ni-Al-enriched nanoparticles were visualized by the use of the 30% (Ni+Al) isoconcentration surfaces. The equivalent spherical particle radius, R , was determined by [28]:

$$R = \left(\frac{3}{4\pi} \frac{n\Omega}{\zeta} \right)^{\frac{1}{3}} \quad (1)$$

where n is the number of atoms in the particle defined by the isoconcentration surfaces, $\Omega = 1.201 \times 10^{-2} \text{ nm}^3$ is the atomic volume of bcc Fe, and $\zeta = 0.37$ is the overall detection and reconstruction efficiency. The particle number density, N , were calculated from [28]:

$$N = \frac{N_p \zeta}{n_{total} \Omega} \quad (2)$$

where N_p is the number of fully-contained plus 50% of the partially-contained particles within the volume, n_{total} the total number of atoms detected in the same volume. The volume fraction of the particles was obtained through dividing the total volume inside the isoconcentration surfaces by the specimen volume.

The density functional theory (DFT) based first-principles calculations were performed by the Vienna ab initio Simulation Package (VASP) [2630]. Ultrasoft pseudopotentials (US-PP) implemented in VASP were adopted, and the generalized gradient approximation (GGA) was used to describe the electronic exchange and correlation [2731]. A three-dimensional 128-atom periodic supercell with $4 \times 4 \times 4$ unit cells was used to determine the total energy, with a plane-wave energy cutoff 400 eV and $1 \times 1 \times 1$ Γ -centered Monkhorst-Pack grids. Equilibrium cell volumes and all internal atomic positions of the supercells were fully relaxed until convergence with the total energy tolerance of 10^{-4} eV.

3. Results

3.1 Mechanical properties

Hardness measurements were conducted to evaluate the age hardening response of the Fe-5Ni-1Al- x Mn alloys with different Mn contents. The microhardness of the 0-5Mn alloys is shown in Fig. 1 as a function of aging time at 550 °C. The hardness of the Fe-5Ni-1Al alloy without any Mn additions ~~shows no appreciable changes~~increases slightly from 201±10 to 210±11 HV during the first 30 min. aging period, and gradually reaches peak values of 280±15 HV at an aging time of 6 h, indicating a slow age hardening kinetics [22]. For the 1 Mn alloy, the as-quenched hardness reaches 238±17 HV, which is mainly due to the solid-solution hardening and grain-size refinement induced by Mn, as indicated by Ref. 22. Upon aging, the 1Mn alloy shows a moderate increase in hardness within the first 30 min. of aging and then exhibits a dramatic increase to peak hardness values of 366±17 HV after 2 h aging, resulting in a pronounced increase in hardness (~128 HV) as compared with the as-quenched sample. When the Mn contents increases to 3 wt.%, the hardness of the alloy increases rapidly to 436±13 HV after aging for 30 min. and reaches peak hardness values of 456±15 HV after aging for 2 h, followed by a gradual decline [22]. With a further increase of Mn content to 5 wt.%, the hardness profile shows a similar trend as observed for the 3Mn alloy. It is interesting to note that the hardness of the 5Mn alloy is slightly higher than that of the 3Mn alloy during the first 8 h aging period, but after that, its hardness becomes lower than that of the 3Mn alloys, indicating a relatively faster aging kinetics of the 5Mn alloy, as compared with the 3Mn alloy. The above hardness measurements demonstrate that the Mn additions remarkably accelerate the aging kinetics, shifting the hardness peak towards shorter periods of time. In addition, Mn plays an important role in enhancing the age-hardening response of the Fe-Ni-Al-Mn alloy, and its beneficial effect becomes near-saturated when the Mn content reaches 3 wt.%.

Room-temperature tensile tests were performed to further investigate the effects of Mn on the mechanical properties of the Fe-5Ni-1Al-xMn alloys. Since the 1Mn, 3Mn and 5Mn alloys reach their peak aging in 2 h at 550 °C, the tensile tests were performed on all the samples after aging for 2 h at 550 °C. The representative engineering stress-strain curves of the alloys ~~after aging for 2 h at 550 °C~~ are presented in Fig. 2a, and the yield strength, ultimate tensile strength, uniform elongation, elongation-to-failure and reduction in area are summarized in Table 2. At an aging time of 2 h, the 0Mn alloy shows a yield strength of 556 ± 10 MPa and an ultimate tensile strength of 651 ± 15 MPa [22]. The addition of 1 wt.% Mn results in a substantial increase of approximately 300 MPa in both the yield strength and ultimate tensile strength of the alloy, together with a small loss of elongation-to-failure from 20 ± 2 % to 14 ± 2 %. As the Mn content is increased to 3 wt.%, the yield strength and ultimate tensile strength further increases to 1201 ± 18 and 1243 ± 15 MPa, respectively, while the ductility remains nearly unaffected. ~~Accompanying the improved strength, the 3Mn alloy does not show a significant reduction in ductility, exhibiting an elongation-to-failure of 12 ± 2 % and a reduction in area of 51 ± 4 % [22]. Further increasing the Mn addition to 5 wt.%, the yield strength only show a further increase of 79 MPa, as compared with the 3Mn alloy, but the elongation to failure decrease sharply to 6 ± 1 %. Increasing the Mn content to 5 wt. % results in a marginal increase in yield strength to 1280 ± 16 MPa with a decrease in the elongation-to-failure to 6 ± 1 %. More notably, the uniform elongation of the alloys varies significantly with Mn content. As summarized in Fig. 2b, the uniform elongation decreases gradually from 10.5 ± 1.5 % in the 0Mn alloy to 6.5 ± 1.4 % in the 3Mn alloy but then drops significantly to 0.7 ± 0.5 % in the 5Mn alloy.~~

Furthermore, ~~t~~T_o experimentally determine the effect of Mn on the age hardening response of the Fe-5Ni-1Al-xMn alloy, the as-quenched specimens of these alloys with different Mn

contents were also tested. Their tensile properties are also included in Table 2, and the age hardening response of the alloys after aging for 2 h at 550 °C are presented in Fig. 2b. The increment in yield strength of the 0Mn, 1Mn, 3Mn and 5Mn alloys are 127 ± 19 , 396 ± 21 , 519 ± 28 and 595 ± 28 MPa, respectively, demonstrating that Mn significantly enhances the age-hardening response of the Fe-Ni-Al-Mn alloy, in consistent with the hardness measurements. In addition, the uniform elongation of the alloys aged for 2 h at 550 °C varies significantly with Mn content, decreasing gradually from 10.5 ± 1.5 % in the 0Mn alloy to 6.5 ± 1.4 % in the 3Mn alloy followed by a significant drop to 0.7 ± 0.5 % in the 5Mn alloy (Fig. 2c).

3.2 Fracture surfaces

The fracture surfaces of the Fe-5Ni-1Al-xMn alloys after aging for 2 h at 550 °C are shown in Fig. 3. For the alloys with 0-3 wt.% Mn, the ~~age-hardening effect does~~ Mn additions do not induce a significant change in fracture mode, and all the three alloys show obvious necking and a lot of fine dimples (Fig. 3a-c), indicating a characteristic mode of a ductile fracture. As the Mn content increases to 5 wt.%, the fracture mode changes to a mixed fracture mode, with cleavage facets observable in areas otherwise consisting of dimpled rupture or intergranular fracture (Fig. 3d). The enlarged views of representative areas in the red and yellow rectangles in Fig. 3d are illustrated in Fig. 3e and f, respectively. The near edge of the fracture surface (Fig. 3e) shows brittle failure revealing the quasi-cleavage facets and intergranular cracks, together with a small amounts of dimples. In comparison, in the center region (Fig. 3f), the fracture surface consists mainly of large cracks and ductile dimples. It is interesting to note that although the 5Mn alloy exhibits only a little uniform elongation (less than 1%), the fracture sample shows an obvious necking with a large reduction in area ($\sim 40 \pm 5$ %).

3.3 APT characterization of the precipitation microstructures

To attain precise information about the nanoscale precipitation process, APT investigations were performed on the Fe-5Ni-1Al-xMn alloys in the 2 h aged condition. ~~The 30% (Ni+Al) concentration isosurfaces were used to visualize the Ni-Al-enriched nanoparticles.~~ The ~~precipitation microstructures of Ni-Al-enriched nanoparticles in~~ the 0Mn, 1Mn, 3Mn and 5Mn alloys after aging for 2 h at 550 °C are presented in Fig. 4a-d, respectively. Although spheroidal Ni-Al-enriched nanoparticles are detected readily in all alloys, their ~~precipitation microstructures~~ size and number density vary significantly with Mn addition. The 0Mn alloy contains a very small ~~amount~~ number density of Ni-Al-enriched nanoparticles, whereas high number densities of nanoparticles can be observed in the Mn-containing alloys. In particular, a considerable ~~amount~~ number density of coarse particles with sizes of larger than 6 nm appear in the 5Mn alloy.

The size distributions of the Ni-Al-enriched nanoparticles in the Fe-5Ni-1Al-xMn alloys with different Mn additions are shown in Fig. 5. ~~The size distribution of the nanoparticles shifts gradually to smaller particle sizes as the Mn content increases from 0 to 3 wt.%, but then shifts to slightly larger particle sizes with the Mn content further increasing to 5 wt.%. The average particle radius of the Ni-Al-enriched nanoparticles decreases from 2.2±0.4 nm for the 0Mn alloy to 1.9±0.7 nm for the 1Mn alloy and further to 1.4±0.3 nm for the 3Mn alloy, but then increases to 1.7±0.6 nm for the 5Mn alloy.~~ The statistical information, including the average particle radius, number density and volume fraction, is summarized in Fig. 6 as a function of Mn content. The variation of the average particle radius and number density of the Ni-Al-enriched nanoparticles with Mn content exhibits a rather complicated behavior, rather than a monotonic behavior as observed for the variation of the volume fraction. ~~The average particle radius of the Ni-Al-~~

~~enriched nanoparticles decreases from 2.2 ± 0.4 nm for the 0Mn alloy to 1.9 ± 0.7 nm for the 1Mn alloy and further to 1.4 ± 0.3 nm for the 3Mn alloy, but then increases to 1.7 ± 0.6 nm for the 5Mn alloy.~~ Conversely, ~~the~~ The number density of the Ni-Al-enriched nanoparticles increases from $1.7 \pm 0.5 \times 10^{22} \text{ m}^{-3}$ for the 0Mn alloy to $2.9 \pm 0.3 \times 10^{23} \text{ m}^{-3}$ for the 1Mn alloy and further to $8.6 \pm 0.6 \times 10^{23} \text{ m}^{-3}$ for the 3Mn alloy, but then drops slightly to $7.5 \pm 0.4 \times 10^{23} \text{ m}^{-3}$ for the 5Mn alloy. In comparison, the volume fraction of the Ni-Al-enriched nanoparticles increases monotonically with the increasing Mn content, from 0.08 ± 0.01 % for the 0Mn alloy to 0.82 ± 0.04 % for the 1Mn alloy and to 0.95 ± 0.02 % for the 3Mn alloy and further to 1.57 ± 0.06 % for the 5Mn alloy. These observations are consistent with the study by Kapoor et al. [9] on the Fe-Cu-Ni-Al-Mn alloys. It is found that Mn partitions to the NiAl-type nanoparticles by occupying the Al sublattice, leading to the formation of the B2-ordered Ni(Al,Mn) nanoparticles [8,9,20-22,25]. As the atomic radius of Mn is smaller than that of Al, Mn substitution would result in a better lattice mismatch with the bcc Fe matrix and hence a smaller nucleation barrier for the formation of NiAl-type nanoparticles, which dramatically increases the number density and volume fraction of the nanoparticles [9,22].

3.3 APT composition of the Ni-Al-enriched nanoparticles

The quantification of the solute partitioning between the nanoparticles and the matrix was determined from proximity histograms [2832], in which the average 3 dimensional compositional information with respect to the distance from the particle/matrix interface is presented. The proximity histograms of the Ni-Al-enriched nanoparticles in 0Mn, 1Mn, 3Mn and 5Mn alloys after aging for 2 h at 550 °C are illustrated in Fig. 7a-d, respectively, and the quantitative analysis of the particle compositions is summarized in Fig. 8. In the 0Mn alloy (Fig. 7a), the

partitioning of Fe to the matrix and the partitioning of Ni and Al to the nanoparticles are clearly evident. However, these nanoparticles are not pure NiAl but contain significant amounts of Fe, and additionally, Ni (41.2±6.3 at.%) exhibits a slightly higher than stoichiometric degree of partitioning as compared with Al (37.0±5.6 at.%) in these nanoparticles, which may be due to the higher concentration of Ni (4.7 at.%) compared to Al (2.1 at.%) in the alloy. In comparison, in the Mn-containing alloys (Figs. 7b-d), the concentration profiles of all Ni, Al and Mn increase monotonically with the distance towards the center of the nanoparticles. The right extreme cutoff of the distance scale reflects the approximate center of the particles. The degree of the Ni partitioning in the nanoparticles does not change noticeably among the alloys with 0-5 wt.% Mn, remaining at a level of 37-42 at.%, whereas that of both Al and Mn vary significantly with Mn content. The Al concentration decreases from 37.0±5.6 at.% in the 0Mn alloy to 30.7±1.9 at.% in the 1Mn alloy and further to 24.1±3.1 at.% in the 3Mn alloy, but then shows no discernible changes with further increasing Mn content to 5 wt.%. By contrast, the Mn concentration in the Ni-Al-enriched nanoparticles increases monotonically with the Mn content in the alloys, from nearly zero in the 0Mn alloy to 17.2±5.5 at.% in the 5Mn alloy. It is interesting to note that the atomic ratios of Ni:(Al+Mn) in the 0Mn, 1Mn, 3Mn and 5Mn alloys are 1.10, 1.04, 1.12, 0.94, respectively, suggesting that Mn essentially occupies the Al site in the Ni-Al-enriched nanoparticles, ~~in~~-consistent with previous experimental and simulation results in the Fe-Ni-Al-Mn-based alloys [~~16,17,20,21~~8,9,20-22,25]. More interestingly, the concentration of Al and Mn at the center of the nanoparticles in the 5Mn alloy is almost equal, both being approximately 25 at.%, and their sum is close to the Ni concentration, suggesting the formation of a new type of nanoparticles with a composition of Ni₂AlMn. It is known that Ni₂AlMn is Heusler phase with an L2₁-ordered crystal structure, which is a further ordering of Al and Mn atoms on the Al

sublattice of the B2-ordered structure [29,33]. Similar L2₁-ordered nanoparticles with a composition of Ni₂AlTi have also been found in several Fe-Ni-Al-Ti-based ferritic alloys recently, which is reported to be effective in improving strength of the alloys at elevated temperatures [30,31,34,35].

As the compositional measurements obtained with the proximity histogram method average over all isoconcentration surfaces within the analyzed volume, the proximity histograms in Fig. 7 reflects the statistical composition of all particles in Fig. 3. In order to explore the key factors governing the formation of the NiAl- and Ni₂AlMn-type particles in these alloys with different Mn contents, the effect of both the Mn content and particle size on the composition of the nanoparticles were analyzed. Considering that the 1Mn and 5Mn alloys show a relatively wide size distribution of nanoparticles, ranging from ~0.5 to ~5 nm in radius (see Fig. 5), the compositions of both fine (less than 3 nm in diameter) and coarse (larger than 6 nm in diameter) nanoparticles in the 1Mn and 5Mn alloys were analyzed separately. The representative groups of nanoparticles (pink particles) and their corresponding proximity histograms are shown in Fig. 9. In addition, 1-nm-thick atom maps through the centers of representative nanoparticles in each group are also included in Fig. 9, in which the relative positions and extents of the Al (cyan), Ni (red) and Mn (blue) atoms are indicated.

For the group of fine particles with sizes of less than 3 nm in the 1Mn alloy (Fig. 9a), Ni exhibits a slightly higher than stoichiometric degree of partitioning relative to Al, and the Mn concentration is only ~6 at.% at the center of the particles. As the particle size increases to ~8 nm in the 1Mn alloy (Fig. 9b), the Mn concentration shows a slight increase but is still below ~10 at.% at the center of the particle. The Ni:Al:Mn ratio of the largest particle in the 1Mn alloy is ~4:3:1, indicating it is still a NiAl-type particle with Mn occupying the Al site. For the group of fine

particles with sizes of less than 3 nm in the 5Mn alloy (Fig. 9c), the Mn concentration increases to ~12 at.% but is still approximately half of the Al concentration, implying that these fine particles in the 5Mn alloys are still of NiAl-type. In contrast, the group of coarse particles in the 5Mn alloy shows an almost equal concentration of Al and Mn, and the Ni:Al:Mn ratio is approximately 2:1:1 at the center of the particles, a characteristic of the Ni₂AlMn-type particles. In addition, the center of these Ni₂AlMn-type particles is lean in Fe and other impurities (~2 at.%), suggesting that the composition of the particle core is close to the equilibrium composition of Ni₂AlMn. To further examine the equilibrium nature of the Ni₂AlMn-type particles in the 5Mn alloy, the composition of the matrix was determined from the regions far away from the interface in the proximity histograms, and the concentration of Ni, Al and Mn in the matrix are determined to be 4.0 ±0.1, 1.9±0.1, and 4.2±0.1 at.%, respectively. In view of the limited solubility of Ni and Mn in the bcc Fe-matrix (~4 at.% in total at 550 °C) [1722], the matrix remains in a supersaturated state. Therefore, the existence of the near-stoichiometric Ni₂AlMn nanoparticles in a supersaturated bcc-Fe matrix further supports that the Ni₂AlMn-type nanoparticles are a stable phase in the 5Mn alloy. It is interesting to point out that the precipitation of Ni₂AlMn-type nanoparticles at a position of $z = \sim 70$ nm along the major distance axis in Fig. 9d is likely to be grain-boundary precipitation. In APT, grain boundaries are normally observed by the solute segregation to the plane of the grain boundaries. However, no significant solute segregation was observed along this plane in the current study. Nevertheless, the interesting precipitation behavior of Ni₂AlMn nanoparticles in Fig. 9d is worthy of a detailed study on the grain-boundary microstructure of the 5Mn alloy using the lift-out method in the future. Furthermore, the Ni₂AlMn-type phase is found only in the coarse particles in the 5Mn alloy, and the fine particles in the 5Mn alloy and all particles in the 1Mn alloy are of NiAl-type,

indicating that the Ni₂AlMn-type nanoparticles are essentially formed as a result of the coarsening of the NiAl-type nanoparticles and the transformation is related not only with the particle size but also the Mn content in the alloy.

4. Discussion

The above results shows that the precipitation microstructure and mechanical properties of the Fe-Ni-Al-Mn alloys vary significantly with the Mn content. In the following sections, the mechanism of the precipitate transformation from NiAl-type to Ni₂AlMn-type and its influence on the mechanical properties of the alloys will be discussed in details.

4.1 Mechanism of the precipitate transformation from NiAl-type to Ni₂AlMn-type

Basically, the precipitate transformation is governed by the competition of driving forces for the nucleation and stability of the precipitates before and after the transformation [4213]. In this study, the mechanism for the transformation from NiAl-type to Ni₂AlMn-type will be discussed from both energetic and kinetic points of view.

First, the energetic origin for the transformation from NiAl-type to Ni₂AlMn-type was explored using the first-principles calculations. The calculations were performed in the 128-atom supercells of B2-NiAl and L2₁-Ni₂AlMn, and the schematic crystal structures are presented in Fig. 10. The precipitation energies of the B2-Ni₆₄Al₆₄ and Heusler Ni₆₄Al₃₂Mn₃₂ structures were calculated according to the following equations, respectively:

$$E_{NiAl} = (E_{Ni_{64}Al_{64}} - 64\mu_{Ni} - 64\mu_{Al}) / 128, \quad (43)$$

$$E_{Ni_2AlMn} = (E_{Ni_{64}Al_{32}Mn_{32}} - 64\mu_{Ni} - 32\mu_{Al} - 32\mu_{Mn}) / 128, \quad (24)$$

where $E_{Ni_{64}Al_{64}}$ and $E_{Ni_{64}Al_{32}Mn_{32}}$ are the total energies of the $Ni_{64}Al_{64}$ and $Ni_{64}Al_{32}Mn_{32}$ supercells, respectively, and μ_{Ni} , μ_{Al} , and μ_{Mn} are the chemical potentials of Ni, Al, and Mn in dilute bcc Fe solid solution, respectively. Based on the first-principles total energy calculations in the 128-atom supercells, the precipitation energies of the B2- $Ni_{64}Al_{64}$ and Heusler $Ni_{64}Al_{32}Mn_{32}$ are determined to be -0.183 and -0.231 eV/atom, respectively, as shown in Fig. 10. The more negative precipitation energy of the $Ni_{64}Al_{32}Mn_{32}$ structure indicates that the Ni_2AlMn phase is structurally more stable than the NiAl phase and the structural transformation from the NiAl-type to the Heusler Ni_2AlMn -type is energetically favorable.

Second, the kinetic origins of the transformation from NiAl-type to Ni_2AlMn -type were examined. It is known that the kinetics of precipitation from a supersaturated solid solution is governed by the nucleation and growth rates of the precipitates. Thus, it is critical to comparatively assess ~~to~~ both the nucleation and growth behavior of the NiAl- and Ni_2AlMn -type nanoparticles in the Fe-based alloys. From the nucleation point of view, strain energy is known to play an important role in determining the critical energy for the formation of coherent precipitates [~~42~~13]. It has been experimentally determined that the lattice constant of the bcc-Fe and B2-NiAl phases and half of the lattice constant of the Heusler Ni_2AlMn phases are 0.2866 [~~32~~36], 0.2886 [~~33~~37], and 0.2912 nm [~~34~~38], respectively. Thus, both B2-NiAl and Heusler Ni_2AlMn satisfy the lattice coherent requirement in the bcc-Fe matrix. However, the formation of the Ni_2AlMn nanoparticles would induce a larger lattice misfit strain with the bcc-Fe matrix, as compared with the NiAl nanoparticles, resulting in a relatively high strain energy for the nucleation of the Ni_2AlMn nanoparticles. In other words, it is more difficult for the Ni_2AlMn nanoparticles to nucleate from the bcc-Fe matrix, as compared with the NiAl nanoparticles. In

addition, from the growth point of view, the growth of the nanoparticles is accomplished by the diffusion of the constitute elements through the matrix. It has been found that the diffusion coefficient of Mn in bcc-Fe ($2.26 \times 10^{-19} \text{ m}^2/\text{s}$) is significantly lower than that of Ni ($3.61 \times 10^{-20} \text{ m}^2/\text{s}$) and Al ($5.71 \times 10^{-19} \text{ m}^2/\text{s}$) at 550 °C [3539]. Considering the high fraction of Mn atoms necessary for the Ni₂AlMn-type nanoparticles, the slow diffusion coefficient of Mn would lead to a slow growth rate of the Ni₂AlMn-type nanoparticles, as compared with the NiAl-type nanoparticles with a minor amount of Mn contents.

From the above discussion, it is clear that the first-principles calculations provide critical information on the structural stability of the NiAl and Ni₂AlMn phases and explain the precipitate transformation from NiAl-type to Ni₂AlMn-type. However, these calculations cannot predict the nucleation sequence of the two types of nanoparticles due to the complex nature of nucleation processes in multi-component alloys. Our analysis indicates that the Ni₂AlMn-type nanoparticles have both slow nucleation and growth kinetics, as compared with the NiAl-type nanoparticles, leading to the formation of a high number densities of NiAl-type nanoparticles, rather than the Ni₂AlMn-type nanoparticles, at the early stage of precipitation. However, the Ni₂AlMn-type nanoparticles are energetically more favorable than the NiAl-type nanoparticles, the first formation of the NiAl-type nanoparticles would transform to the Ni₂AlMn-type nanoparticles at later stages of precipitation, accompanying with the Mn diffusion from the matrix into the nanoparticles.

4.2 Effects of the NiAl-to-Ni₂AlMn transformation on the precipitation strengthening

It is commonly understood that the degree of nanoparticle strengthening is strongly dependent upon the size, number density, and micro-mechanical properties of the nanoparticles

as well as the nature of the nanoparticle interaction with the dislocations. APT reveals that the Mn additions not only influence the size and number density of the nanoparticles but also lead to the phase transformation of the nanoparticles; thus, it is critical to quantitatively understand the effect of the precipitate transformation from NiAl-type to Ni₂AlMn-type on the strengthening response of the Fe-based alloys. As the Ni₂AlMn-type phase is found only in the coarse particles in the 5Mn alloy, it is speculated that the Ni₂AlMn-type nanoparticles are essentially formed as a result of the coarsening of NiAl-type nanoparticles. The interesting nucleation and growth behavior of the 5Mn alloy is worthy of further studies to develop a comprehensive understanding of the precipitation pathway of the NiAl- and Ni₂AlMn-type nanoparticles in multi-component alloys. As the ~~NiAl to Ni₂AlMn transformation only occurs~~ coexistence of the NiAl- and Ni₂AlMn-type nanoparticles is found only in the 5Mn alloy, the focus of the strengthening modelling was placed on the NiAl- and Ni₂AlMn-type nanoparticles in the 5Mn alloy. Based on the compositional analysis in Fig. 9c and d, the NiAl- and Ni₂AlMn-type nanoparticles are categorized by the particle size (less and larger than 6 nm, respectively). The average size and number density of the NiAl- and Ni₂AlMn-type nanoparticles are summarized in Table 3. For the NiAl-type nanoparticles with an average size (2.3 ± 0.9 nm, see Table 3) below the critical one for the Orowan looping, the particle shearing mechanism for dislocation motion is expected to be active, while for the Ni₂AlMn-type nanoparticles with a large particle size (7.2 ± 1.4 nm in average, see Table 3) and high hardness, the Orowan by-pass mechanism is expected to be operative [3640].

For the particle shearing mechanism of the NiAl-type nanoparticles, the increase in yield strength results mainly from the contributions of order strengthening ($\Delta\sigma_{order}$), coherency

strengthening ($\Delta\sigma_{coherency}$), and modulus strengthening ($\Delta\sigma_{modulus}$). The equations for these contributions are given by [37,38,41,42]

$$\Delta\sigma_{order} = M \left(\frac{\gamma_{apb}}{b} \right)^{3/2} \left(\frac{4r_s f}{\pi T} \right)^{1/2}, \quad (35)$$

$$\Delta\sigma_{modulus} = M \frac{Gb}{L} \left[1 - \left(\frac{E_p}{E_m} \right)^2 \right]^{\frac{3}{4}}, \quad (46)$$

$$\Delta\sigma_{coherency} = 4.1MG\varepsilon^{3/2} f^{1/2} \left(\frac{R}{b} \right)^{1/2}, \quad (57)$$

where $M = 3$ is the Taylor factor, $\gamma_{apb} = 0.5 \text{ Jm}^{-2}$ is average value of the anti-phase boundary energies of NiAl [36,40], $b = 0.25 \text{ nm}$ is the Burgers vector in the matrix, $r_s = (2/3)^{1/2}R$ is the average particle radius in the glide plane [37,41], f is the volume fraction of the NiAl-type nanoparticles, which can be estimated by $f=4/3\pi R^3 N$, where R and N are the nanoparticle radius and number density, respectively, T is the line tension of the dislocation, usually taken to be $Gb^2/2$ [37,41], where $G = 80 \text{ GPa}$ is the shear modulus of the matrix, $\varepsilon = 2/3(\Delta a/a)$ is the constrained lattice parameter mismatch, with $\Delta a/a \approx 0.002$ as the lattice parameter mismatch between the NiAl-type nanoparticles and matrix [39,43], L is the mean particle spacing in the slip plane and can be calculated from the equation $L=0.866/(RN)^{1/2}$ [37,41], and E_p and E_m are the dislocation line energy in the matrix and the nanoparticles, respectively [38,42]. As described in more details in Ref. [40,44], the ratio of E_p/E_m depends on the nanoparticle radius R and is calculated to be 0.983 in this study. On reasonable assuming that the contributions due to all these factors are additive, the overall precipitation strengthening of the NiAl-type nanoparticles can be calculated by $\Delta\sigma_{NiAl} = \Delta\sigma_{coherency} + \Delta\sigma_{order} + \Delta\sigma_{modulus}$. Using the experimental data $R = 1.65 \text{ nm}$ and $N = 7.2 \times 10^{23} \text{ m}^{-3}$, as determined by APT, the strengthening contributions from the order strengthening, modulus strengthening, and coherency strengthening are determined to be ~399,

~155, and ~26 MPa, respectively, and the overall strengthening from the NiAl-type nanoparticles are ~580 Mpa, as summarized in Fig. 11.

Coarse Ni₂AlMn-type particle (7.2±1.4 nm) are known to be hard particles and would strengthen the steels by Orowan looping. The corresponding strengthening effect can be described by the Ashby-Orowan relationship as given by [4445]

$$\Delta\sigma_{Ni_2AlMn} = 0.84M \left(\frac{1.2Gb}{2\pi L} \right) \ln\left(\frac{\lambda}{2b}\right) , \quad (68)$$

where M , G , b , and L are the Taylor factor, shear modulus of the matrix, Burgers vector, and mean particle spacing in the slip plane, respectively, and $\lambda = 2(2/3)^{1/2}R$ is the outer cut off distance [4445]. Using the APT data of the Ni₂AlMn-type nanoparticles, $R = 3.60$ nm and $N = 1.4 \times 10^{22} \text{ m}^{-3}$, the strengthening contributions from the Orowan looping of the Ni₂AlMn-type nanoparticles is determined to be ~194 ~~Mpa~~MPa (Fig. 11).

To calculate the overall precipitation strengthening effect from both the NiAl- and Ni₂AlMn-type nanoparticles ($\Delta\sigma_{total}$), the strengthening effects of the two types of nanoparticles are superimposed according to the general formulation as given by [4445]

$$\Delta\sigma_{total} = \sqrt{\Delta\sigma_{NiAl}^2 + \Delta\sigma_{Ni_2AlMn}^2} . \quad (79)$$

Based on the above calculations, the total increment in yield strength due to both the NiAl- and Ni₂AlMn-type nanoparticles is ~612 MPa, which is close to the observed experimental value of 595±28 MPa (Fig. 11). In addition, the above analysis also indicates that although the hard Ni₂AlMn-type nanoparticles has a higher strengthening efficiency than the NiAl-type nanoparticles, they make a minor contribution to the total strengthening effects, as compared with the NiAl-type nanoparticles, due mainly to their small number density.

4.3 Effects of the NiAl-to-Ni₂AlMn transformation on the alloy ductility

As shown in Fig. 2, all alloys with 0-3 wt.% Mn exhibit a good ductility with the uniform elongation ranging from 6.5% to 10.5%. However, as the Mn content increases to 5 wt.%, the uniform elongation drops significantly to less than 1%. Concomitant with this decrease in ductility, a transition in fracture mode was observed from predominantly transgranular dimpled fracture to a mixed one containing brittle quasi-cleavage facets, intergranular facets and a small amount of dimples, as shown in Fig. 3. APT reveals that the average radius of the NiAl-type nanoparticles increases from ~1.4 nm in the 3Mn alloy to ~1.7 nm in the 5Mn alloy. However, it is unlikely that such a small difference in particle size would significantly impair the ductility, and a good ductility with uniform elongation of >5% is often achieved in other NiAl-strengthened steels with a similar or higher strength, in which the average radius of the NiAl-type nanoparticles (1.6-1.7 nm) is similar to that in the 5Mn alloy (~1.7 nm) [21,42,25,46].

Another distinct difference between the 3Mn and 5Mn alloys in microstructure is the formation of the coarse Ni₂AlMn-type nanoparticles in the 5Mn alloy. It is well known that Ni₂AlMn is a hard Heusler phase, whose hardness (>6 GPa) is approximately twice that of the NiAl phase (~3 GPa) [43,47]. However, Ni₂AlMn is extremely brittle and exhibits limited plastic flow. Stress concentration and fine cracks easily form in these brittle nanoparticles sustaining a high stress, and for the 5Mn alloy with a body-centered cubic (bcc) structure, the transgranular cracks are prone to propagate along specific cleavage planes, leading to the cleavage-like fracture and significantly decreasing the alloy ductility [48]. In addition, as the grain-boundary diffusion is much faster than the volume diffusion, grain boundaries are expected to be favored sites for the precipitation and growth of Ni₂AlMn particles. The grain-boundary precipitation of brittle Ni₂AlMn-type nanoparticles would also embrittle the alloy and promote the intergranular cracking. The precipitation of Ni₂AlMn-type at a position of $z = \sim 70$ nm along the major distance

axis in Fig. 9d is likely to be grain-boundary precipitation. In addition, the large cracks in Fig. 3d-f are probably due to the delaminating along the large precipitate bands. Therefore, the brittle Ni_2AlMn -type nanoparticles would embrittle the 5Mn alloy by promoting both cleavage fracture and intergranular cracking. As a result, both brittle quasi-cleavage and intergranular facets can be observed from the fracture surface of the 5Mn alloy (Fig. 3d-f).

5. Summary

Based on the systematic study of the precipitate transformation from NiAl-type to Ni_2AlMn -type and its influence on the mechanical properties of the Fe-Ni-Al-Mn-based alloys, the following conclusions are drawn:

1. APT reveals that the Mn plays an important role not only in increasing the number density of the NiAl-type nanoparticles but also in promoting the formation of the Ni_2AlMn -type nanoparticles. Although the Ni_2AlMn -type nanoparticles are energetically more favorable than the NiAl-type nanoparticles, as determined by from the FP calculations, their nucleation and growth kinetics are comparatively slow. As a result, the NiAl-type nanoparticles precipitate out first and then transform to the Ni_2AlMn -type nanoparticles at a later stage of precipitation growth, in particular along grain boundaries.
2. The degree of nanoparticle strengthening is dependent not only upon the property of the nanoparticles but also their size and number density. In the 5Mn alloy, although the hard Ni_2AlMn -type nanoparticles have a higher strengthening efficiency than the NiAl-type nanoparticles, they make a minor contribution to the total strengthening effects due to both their large particle size and small number density.

3. The formation of the ~~hard and brittle Ni₂AlMn-type Heusler particles~~ Ni₂AlMn-type nanoparticles with a composition consistent with that of the Heusler phase are likely to promotes the brittle cleavage and intergranular fracture of the 5Mn alloy, thereby resulting in a significantly decrease of the alloy ductility. Concomitantly, the fracture mode is transformed from predominantly transgranular dimpled fracture to a mixed one containing brittle quasi-cleavage facets, intergranular facets and a small amount of dimples.
4. The Mn content plays an important role in determining the mechanical properties of the Fe-Ni-Al-Mn-based alloys. With an appropriate amount of Mn (~3 wt.%), a good combination of high strength and high ductility can be achieved in the Fe-based alloys strengthened by Ni(Al,Mn) nanoparticles.

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Graphical Abstract

Table 1. Alloy compositions of Fe-Ni-Al-Mn alloys (weight percent and atomic percent).

		Ni	Al	Mn	Fe
0Mn	wt. %	5.0	1.0	-	94.0
	at. %	4.7	2.1	-	93.2
1Mn	wt. %	5.0	1.0	1.0	93.0
	at. %	4.7	2.0	1.0	92.3
3Mn	wt. %	5.0	1.0	3.0	91.0
	at. %	4.6	2.0	2.9	90.5
5Mn	wt. %	5.0	1.0	5.0	89.0
	at. %	4.5	2.0	4.8	88.7

Table 2. The yield strength (YS), ultimate tensile strength (UTS), elongation-to-failure (EL), and reduction in area (RA) for the 2 h aged and as-quenched (AQ) alloys.

	YS (MPa)	UTS (MPa)	EL (%)	RA (%)
0Mn, 2 h	556±10	651±15	20±2	85±3
1Mn, 2 h	869±11	942±15	14±2	62±5
3Mn, 2 h	1201±18	1243±15	12±2	51±4
5Mn, 2 h	1280±16	1308±18	6±1	40±5
0Mn, AQ	429±9	512±10	22±2	88±2
1Mn, AQ	473±10	566±14	17±2	83±3
3Mn, AQ	682±10	777±17	14±3	58±5
5Mn, AQ	685±12	799±15	11±3	55±5

Table 3. Average diameters and number densities of NiAl- and Ni₂AlMn-type nanoparticles in the 5Mn alloy.

<u>Particle</u>	<u>Average diameter (nm)</u>	<u>Number density (m⁻³)</u>
<u>NiAl-type</u>	<u>2.3±0.9</u>	<u>7.2×10^{23}</u>
<u>Ni₂AlMn-type</u>	<u>7.2±1.4</u>	<u>1.4×10^{22}</u>

Fig. 1. Hardness as a function of aging time for the 0Mn, 1Mn, 3Mn and 5Mn alloys.

Fig. 2

Fig. 2. (a) Room-temperature tensile stress-strain curves for the 0Mn, 1Mn, 3Mn and 5Mn alloys aged for 2 h at 550 °C, and (b) increases in yield strength of these alloys after aging for 2 h at 550 °C (relative to the as-quenched samples), and (c) the uniform elongation and age hardening response-uniform elongation of these alloys after aging for 2 h at 550 °C.

Fig. 3. Room-temperature fracture surfaces of the alloys aged for 2 h at 550 °C: (a) 0Mn, (b) 1Mn, (c) 3Mn, and (d-f) 5Mn. (e) and (f) show the enlarged views of the red and yellow rectangles in Fig. 3d, respectively.

Fig. 4. 30% (Ni + Al) concentration isosurfaces of the alloys aged for 2 h at 550 °C: (a) 0Mn, (b) 1Mn, (c) 3Mn, and (d) 5Mn. The direction of evaporation is horizontal, from right to left.

Fig. 5. Particle size distributions of the Ni-Al-enriched nanoparticles in the alloys aged for 2 h at 550 °C: (a) 0Mn, (b) 1Mn, (c) 3Mn, and (d) 5Mn.

Fig. 6. (a) Particle radius, (b) number density and (c) volume fraction of the Ni-Al-enriched nanoparticles in the 0Mn, 1Mn, 3Mn, and 5Mn alloys aged for 2 h at 550 °C.

Fig. 7

Fig. 7 (cont'd)

Fig. 7. Proximity histograms of the Ni-Al-enriched nanoparticles in the alloys aged for 2 h at 550 °C: (a) 0Mn, (b) 1Mn, (c) 3Mn, and (d) 5Mn.

Fig. 8. Compositions of the Ni-Al-enriched nanoparticles in the 0Mn, 1Mn, 3Mn, and 5Mn alloys aged for 2 h at 550 °C.

Fig. 9

Fig. 9 (cont'd)

(b)

Fig. 9 (cont'd)

(c)

5Mn, fine particles

Fig. 9 (cont'd)

Fig. 9. Proximity histograms of different groups of nanoparticles in the 1Mn and 5Mn alloys aged for 2 h at 550 °C: (a) fine particles, 1Mn, (b) coarse particles, 1Mn, (c) fine particles, 5Mn, and (d) coarse particles, 5Mn. The inserts show the 1-nm-thick atom maps through the centers of representative nanoparticles in each group. The direction of evaporation is horizontal.

Fig. 10. Atomic structures and calculated precipitation energies of the NiAl- and Ni_2AlMn -type models.

Fig. 11. Calculated strengthening contributions of NiAl- and Ni₂AlMn-type nanoparticles and their overall effect for the 5Mn alloy after aging for 2 h at 550 °C. The experimental value is indicated as a black dot.