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Mechanisms for suppressing discontinuous precipitation and improving mechanical properties of NiAl-strengthened steels through nanoscale Cu partitioning

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Abstract

Control of discontinuous and continuous precipitation is crucial for tailoring the microstructure and mechanical properties of NiAl-strengthened steels. Through a combination of atom probe tomography, transmission electron microscopy, electron backscatter diffraction, first-principles calculations, and mechanical tests, we demonstrate that Cu is effective in not only promoting the nano-scale continuous NiAl precipitation but also in suppressing the coarse-scale discontinuous NiAl precipitation at grain boundaries, which results in the development of new NiAl-strengthened steels with a high yield strength (1400 MPa) and good ductility (10%). Our analyses indicate that the mechanisms for suppressing discontinuous NiAl precipitation are twofold. The main one is the acceleration of continuous NiAl precipitation through Cu partitioning, which swiftly reduces the matrix supersaturation, thereby decreasing the chemical driving force for the growth of discontinuous precipitates. The other is the reduction of grain boundary energy through Cu segregation, which is likely to decrease the nucleation rate of discontinuous precipitates. Consequently, Cu increases the number density of continuous NiAl nanoparticles by more than fivefold, which leads to a twofold enhancement in the strengthening and an improvement in the over-aging resistance of NiAl-strengthened steels. The effects of Cu on the precipitation strengthening mechanisms were quantitatively evaluated.

Keywords: low-carbon steel; discontinuous precipitation; precipitate; precipitation hardening; microstructure formation mechanism

1. Introduction

High-strength low-carbon steels are of considerable technological importance in engineering applications such as automotive, shipbuilding, and energy industries [1-5]. Uniform precipitation of metallic nanoparticles is one of the most effective methods for strengthening low-carbon steels, which allows for the development of advanced steels with high strength, ductility, and weldability [6-10]. Among various potential precipitates used for precipitation strengthening, NiAl is one of the most effective phases [11-17]. The B2-ordered structure of NiAl is a derivative of the body-centered cubic (bcc) structure, and its lattice parameter (~0.2886 nm) is close to that of bcc-Fe (~0.2866 nm) [14]. As such, NiAl precipitates exhibit high coherency with bcc-Fe and can precipitate on a sufficiently fine scale (less than 5 nm in diameter) to provide high a strengthening effect [18-20]. The mechanical properties of NiAl-strengthened steels are highly dependent on the precipitate microstructure, including the size, number density, morphology, and spatial distribution of NiAl precipitates. For achieving the optimal mechanical properties, it is essential to obtain detailed knowledge of the precipitation mechanisms of NiAl-strengthened steels.

NiAl precipitation in steels occurs in two competitive modes, namely continuous precipitation (CP) and discontinuous precipitation (DP) [21-24]. CP refers to the uniform precipitation of spheroidal NiAl nanoparticles, which is associated with continuous changes in the matrix composition [25,26]. By contrast, DP initiates at grain boundaries and proceeds through the cellular growth of alternating plates of NiAl precipitates and solute-depleted matrix behind a moving grain boundary [27-29], which leads to the non-uniform precipitation of coarse-sized NiAl rods near grain boundaries. In the DP reaction, the solute concentration changes abruptly in a narrow region near a growing cell. Studies have shown that both the CP and DP often occur simultaneously in NiAl-strengthened steels [24]. From the strengthening point of view, CP nanoparticles are primarily responsible for precipitation strengthening, whereas DP rods exhibit a limited strengthening capability because of their coarseness and non-uniform distribution. Moreover, DP rods deteriorate the strength of grain boundaries, which results in inferior toughness and fatigue resistance of steels [27,30]. Therefore, minimizing or completely suppressing the DP reaction is crucial for optimizing the mechanical properties of NiAl-strengthened steels. A precipitation reaction can be fundamentally altered by changing the precipitation thermodynamics or varying the precipitation kinetics. Recently, the co-precipitation of NiAl and Cu precipitates in Fe–Ni–Al–Cu-based steels has attracted considerable interest because of their excellent mechanical properties and interesting precipitation processes [17,31-34]. While most studies have focused on the influence of Cu on continuous NiAl precipitation, little research has been conducted on the effect of Cu on discontinuous NiAl precipitation. The strategies and underlying mechanisms for suppressing DP at the grain boundaries of NiAl-strengthened steels remain poorly understood.

In this study, we report that Cu is effective in not only promoting the formation of continuous NiAl nanoparticles in grain interiors but also in suppressing the precipitation of discontinuous NiAl rods along grain boundaries, which leads to the development of new NiAl-strengthened steels with a high yield strength (1400 MPa) and good ductility (10%). The underlying mechanisms of Cu in suppressing DP and promoting CP were systematically studied through a combination of electron microscopies, atom probe tomography (APT), electron backscatter diffraction (EBSD), first-principles calculations, and mechanical tests.

Particular attention was paid to the effects of Cu partitioning on the CP and DP thermodynamics as well as the interaction between the CP and DP processes in the NiAl-strengthened steels.

2. Experimental

Four alloys with nominal compositions of Fe–8Ni–2Al–*x*Cu ($x = 0, 0.5, 1$, and 1.5 wt.%) were prepared by arc-melting a mixture of commercially pure metals (purity > 99.9 wt.%) in a high-purity argon atmosphere. For simplicity, these steels are hereafter referred to as 0Cu, 0.5Cu, 1Cu, and 1.5Cu steels. Steel ingots were melted four times to ensure the chemical homogeneity and drop-cast into the cavity of a copper mold with a dimension of $50 \times 15 \times 3$ mm^3. The as-cast plates were cold-rolled with a total reduction of 67% and solutionized for 30 min at 900 °C, followed by water quenching, and then isothermally aged at 550 °C for different periods of time.

Heat-treated samples were mechanically polished to a final surface finish using 0.05 μm alumina particles and etched for 10–20 s with a 4 vol.% Nital solution, allowing for observation of microstructures via scanning electron microscopy (SEM, FEI Scios). Transmission electron microscopy (TEM) specimens were prepared by ion-milling of mechanically pre-thinned foils to the electron transparent thickness using a precision ion polishing system. TEM and selected area electron diffraction (SAED) measurements were conducted on a JEOL-2100F microscope operated at 200 kV. EBSD specimens were prepared by mechanical polishing down to 0.05 μm, followed by electro-polishing in a solution of HNO_3 (25%) and C_2H_5OH (75%) at a voltage of 20 V at -40 °C. EBSD measurements were performed using a Zeiss Merlin SEM with an Oxford HKL Nordlys detector, and the SEM electron beam was operated at 20 kV and 3.2 nA. Needle-shaped samples required for APT were prepared by lift-out and tip milling in an FEI Scios focused ion beam/scanning electron microscope (FIB/SEM). The APT experiments were performed in a LEAP™ 5000XR. The specimens were analyzed in voltage mode, at 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 0.5% ions per field evaporation pulse. Image Visualization and Analysis Software version 3.8 was used for 3D reconstructions, compositional analyses, and the creation of iso-concentration surfaces.

Hardness measurements were performed under an applied load of 1 kg and a dwelled time of 15 s. For each specimen, at least 8 indents were measured to obtain an average value. Dog-bone shaped tensile specimens with a cross-section of 3.2 × 1 mm^2 and a gauge length of 12.5 mm were prepared by electro-discharge cutting and then carefully ground on each side with SiC papers through 2000 grit. Tensile tests were performed on an MTS tensile machine at a strain rate of 10^{-3} s^{-1}. Yield strength was determined with the 0.2% offset plastic strain method.

First-principles calculations were performed in the framework of density functional theory implemented in the Vienna ab-initio simulation package (VASP) with project augmented wave (PAW) method and the Perdew-Becke-Erzenhof exchange-correlation functional [35-39]. Three-dimensional 128-atom periodic supercells with 4 × 4 × 4 unit cells were used to determine the total energy, with a plane-wave energy cutoff of 450 eV and 4 × 4 × 4 k-point mesh.

3. Results

3.1 DP behavior of Fe-Ni-Al steels

The microstructures of the 0Cu steel in the as-quenched and aged conditions are presented in Fig. 1, in which the DP regions containing coarse-sized NiAl rods exhibit a bright contrast compared to the CP regions consisting of nano-sized NiAl particles. The as-quenched sample (Fig. 1a) exhibits a ferritic structure with irregularly curved grain boundaries, which were formed because of diffusional transformation from austenite to ferrite. After aging for 7.5

min (Fig. 1b), a small area fraction (5% ± 1%) of DP cells are formed along the grain boundaries. As the aging time increases to 30 min (Fig. 1c), additional DP colonies form along grain boundaries, and their growth proceeds into the grain interior regions, which results in an increase in the DP area fraction to 20% ± 4%. The EBSD results (Fig. S1) indicate that the crystallographic orientation of DP colonies is the same as the orientation of the grain from which their growth has started. With a further increase in the aging time to 2 h (Fig. 1d), the DP colonies exhibit a continuous increase in the area fraction to 70% ± 9% and occupy the majority of the microstructure. TEM was used to explore the morphology and crystal structure of rod-like NiAl precipitates in the DP regions. A representative SAED pattern and dark-field TEM (DF-TEM) image of the 0Cu alloy after aging for 2 h at 550 °C are shown in Figs. 1e and f, respectively. The SAED pattern clearly reveals the presence of superlattice reflection corresponding to a B2-ordered phase. The DF-TEM image collected from the 010 superlattice spot depicts the precipitation of rod-like precipitates with diameters of less than 30 nm.

The compositional evolution of DP microstructures was investigated through APT, the required specimens for which were obtained from the DP region by using the site-specific FIB lift-out technique. The DP microstructures of the 0Cu steel after aging for 7.5 min, 30 min, and 2 h are displayed in Figs. 2a, b, c, respectively, in which the relative positions and extents of Ni (green) and Al (cyan) atoms are indicated. In all the three conditions, the partitioning of Ni and Al to rod-like precipitates is clearly evident. The 25 at.% (Ni + Al) isoconcentration surfaces were used to visualize the NiAl precipitates in the DP regions. The NiAl rods are highly oriented and aligned approximately parallel to each other due to the DP reaction. The proximity histogram concentration profiles of Ni, Al, and Fe for the 7.5-min, 30-min, and 2-h aged conditions are illustrated in the right panels of Figs. 2a, b, and c, respectively, and the concentrations of the precipitate core and far-field matrix under these aging conditions are summarized in Tables 1 and 2, respectively. In all conditions, the DP rods are enriched in Ni and Al, together with a small amount of Fe, whereas the matrix is largely depleted in Ni (4.3 at.%) and Al (1.5 at.%) compared with the starting composition (7.5 at.% Ni and 4.1 at.% Al). The NiAl precipitates and matrix in the DP regions exhibit negligible changes in compositions with the aging time.

3.2 Effects of Cu on DP behavior

The SEM microstructures of the 0.5Cu, 1Cu, and 1.5Cu steels in the 7.5-min, 30-min, and 2-h aged conditions are presented in Fig. 3. The area fractions of DP regions in the steels with different Cu contents are displayed in Fig. 4 as a function of aging time. In the 0.5Cu steel, although the DP reaction remains occur, the area fraction of the DP regions decreases drastically, reaching 35% ± 2% after aging for 2 h. As the Cu content increases to 1 wt.%, the area fraction of DP regions further decreases and the DP kinetics slow down. Even after aging for 2 h, only a small area fraction of DP cells (less than 5%) with small sizes was observed near grain boundaries. Further increasing the Cu content to 1.5 wt.% results in complete suppression of the DP reaction, which leads to a homogeneous microstructure and no formation of DP cells at grain boundaries in all aging conditions. The above results indicate that 1.5 wt.% Cu addition is effective in suppressing the DP reaction in the NiAl-strengthened steels.

EBSD measurements were performed to investigate the Cu effects on the grain structure of the Fe-Ni-Al steels (Fig. S2). The average grain size of the 0Cu, 0.5Cu, 1Cu, and 1.5Cu steels in the 2-h aged condition are determined to be 13 ± 10, 12 ± 8, 9 ± 8, and 6 ± 4 μm, respectively. The grain-size refinement by Cu can be attributed to the lowering of the austenite-to-ferrite transformation temperature [33].

3.3 Effects of Cu on CP behavior

Because CP and DP are two competitive processes, we also examined the precipitate microstructural evolution in the CP regions of the 0Cu and 1.5Cu steels. The CP microstructures of the two steels in the different aging conditions are visualized using 25% (Ni + Al) isoconcentration surfaces (Fig. 5). Although near-spheroidal NiAl nanoparticles were detected in both alloys, the particles exhibit considerable differences in the size, number density, and volume fraction. The precipitate radius and volume fraction of the 0Cu and 1.5Cu steels are depicted in Fig. 6 as a function of aging time. In the early stage of precipitation (7.5 min), the average radius, number density, and volume fraction of the NiAl nanoparticles of the 0Cu steel are 0.7 ± 0.3 nm, 9.5×10^{23} m^{-3}, 0.2 ± 0.1%, respectively, whereas those of NiAl nanoparticles of the 1.5Cu steel are 1.0 ± 0.4 nm, 5.0×10^{24} m^{-3}, and 2.1 ± 0.7% (an increase of an order of magnitude in volume fraction relative to the 0Cu steel), respectively. With the increase in aging time, the particle radius and volume fraction increase in both steels. Notably, the particle size and volume fraction of the 1.5Cu steel are larger than those of the 0Cu steel in all the studied conditions. These observations indicate that Cu additions accelerate and promote continuous NiAl precipitation.

To understand the underlying mechanisms of the influence of Cu on the continuous NiAl precipitation, proximity histograms of the 0Cu and 1.5Cu steels were drawn for different aging conditions (Fig. 7). The average compositions of the nanoparticle cores and matrix of the two steels are summarized in Tables 1 and 2, respectively. Ni and Al exhibit local enrichment in the nanoparticles in both steels, and the degree of enrichment increases with the aging time. For the 0Cu steel, the nanoparticles contain 24.1 ± 1.0 at.% Ni, 20.9 ± 1.3 at.% Al, and 55.0 ± 1.5 at.% Fe in the 7.5-min aged condition. With an increase in the aging time, the Ni and Al concentrations increase considerably, whereas the Fe concentration decreases. A nanoparticle composition of 42.6 ± 0.8 at.% Ni, 33.6 ± 0.8 at.% Al, and 23.8 ± 0.7 at.% Fe was observed in the 2-h aged condition. Notably, a strong partitioning of Cu to the NiAl nanoparticles was observed in the 1.5Cu steel. The nanoparticles of the 1.5Cu steel contain 23.7 ± 0.2 at.% Ni, 18.8 ± 0.2 at.% Al, 51.4 ± 0.2 at.% Fe, and a considerable amount of Cu (6.1 ± 0.1 at.%) in the 7.5-min aged condition. The concentrations of Ni, Al, and Cu increase gradually to 44.9 ± 0.9, 33.4 ± 0.8, and 11.0 ± 0.4 at.%, respectively, after aging for 30 min. A further increase of the aging time to 2 h results in no apparent changes in the precipitate composition. In all the studied conditions, the concentrations of Cu in the NiAl nanoparticles are less than 12% and no isolated Cu clusters without the association of NiAl nanoparticles were detected, which indicates that the Cu atoms are enriched in the NiAl nanoparticles rather than forming separate Cu-rich nanoparticles.

3.4 Effects of Cu on grain boundary microstructures

Because the DP reaction initiates at grain boundaries, we examined the grain boundary microstructure to understand the effect of Cu additions on the grain boundary microstructures. Figure 8a displays the atom maps of C, Ni, Al, and Cu of the 1.5Cu steel after aging at 550 °C for 1 min, in which C is an ultra-trace impurity resulting from the raw materials (less than 0.05 at.%). It is documented that carbon atoms tend to segregate at dislocations and grain boundaries of ferritic steels [40-42], and the distribution of carbon atoms can be used to mark dislocations and grain boundaries in APT reconstructions. In this work, we carefully examined the carbon segregation from different angles and found that the carbon segregation exhibits a planar appearance, suggesting that the plane with carbon segregation represents the location of a grain boundary. The co-location of Cu and C at the grain boundary is clearly evident, which strongly indicates that Cu atoms are preferentially segregated at the grain boundaries of the NiAl-strengthened steels at an early stage of aging. At this stage, Ni segregation along the grain boundary was also observed. The quantitative compositional analysis of grain boundary chemistry was conducted using one-dimensional concentration profiles, and the grain boundary chemistry is estimated to be Fe-9.8Ni-4.0Al-4.0Cu-0.8C (at.%). The Cu content in grain interior regions is measured as 1.0 ± 0.3 at.%, and the grain boundary excess of Cu, which represents the number of excess Cu atoms at the grain boundary normalized to its area, is calculated to be approximately 3 atom/nm^2. Using the same method, the grain boundary excess of Ni and C are estimated to be approximately 2.5 and 0.3 atom/nm^2, respectively.

With an increase in the aging time, NiAl precipitation occurs at both the grain interiors and grain boundaries. Figure 8b displays the atom maps of C, Ni, Al, and Cu as well as the 25% (Ni + Al) isoconcentration surfaces of the 1.5Cu steel in the 2-h aged condition. Coarse NiAl nanoparticles form at the grain boundary, along which the layer-like enrichment of Cu is clearly evident. The layer-like enrichment of Cu occurs possibly because of the accumulation of the Cu atoms that originally segregated at the grain boundaries. The proximity histogram analysis indicates that grain-boundary precipitates contain considerably higher Cu concentrations than precipitates in the grain interiors. Importantly, no rod-like discontinuous NiAl precipitates were observed at the grain boundary region, which further confirms the suppression of DP reactions at the nanoscale.

3.5 Mechanical properties

Vickers microhardness measurements were conducted to evaluate the precipitation strengthening responses of the CP and DP precipitates during the aging process. The microhardness profiles of the 0Cu and 1.5Cu steels are depicted in Fig. 9a as a function of aging time. In the as-quenched condition, the 0Cu and 1.5Cu steels exhibit similar hardness values (approximately 230 ± 8 HV and 255 ± 8 HV, respectively). Upon aging, the two steels exhibit different age-hardening responses. For the 0Cu steel containing both CP and DP precipitates, the hardness increases from 230 ± 8 HV to 323 ± 5 HV during the first 7.5-min aging period and reaches a peak value of 400 ± 7 HV after aging for 30 min, which results in a hardness increment of approximately 170 HV as compared with the as-quenched sample. Beyond 30 min, the hardness decreases drastically with the aging time. The hardness decreases to 345 ± 8 HV in the 2-h aged condition and to 278 ± 8 HV in the 32-h aged condition, which indicates a rapid overaging of the precipitates. By contrast, the 1.5Cu steel with high number densities of CP nanoparticles exhibits a sharp increase in hardness in the early stage of age hardening, increasing from 255 ± 8 HV in the as-quenched condition to 415 ± 6 HV in the 7.5-min aged condition. The hardness continues to increase with the aging time and achieves a peak value of 456 ± 6 HV at 2 h of aging, which results in a pronounced age hardening of approximately 205 HV. On further aging, the hardness of the 1.5Cu steel decreases, but with a considerable lower rate than that of the 0Cu steel. The hardness decreases gradually to 420 ± 5 HV after aging for 32 h. In this condition, the 1.5Cu steel still exhibits a high age-hardening response (~80% of that in the peak-aged condition), which indicates that it has a higher overaging resistance than the 0Cu steel.

Room-temperature tensile tests were performed to further investigate the effects of Cu on the mechanical properties of the NiAl-strengthened steels. The engineering stress-strain curves of the 0Cu and 1.5Cu steels in the as-quenched and 2-h aged conditions are depicted in Fig. 9b. The yield strength, ultimate tensile strength, elongation-to-failure, and reduction in area are summarized in Table 3. For the 0Cu steel, the yield strength increases from 621 ± 35 MPa in the as-quenched condition to 925 ± 13 MPa in the 2-h aged condition. Thus, a moderate yield strength increment of approximately 304 MPa is achieved. By contrast, the yield strength of the 1.5Cu steel increases drastically from 698 ± 21 MPa in the as-quenched condition to 1404 ± 10 MPa in the 2-h aged condition, which results in a pronounced age-hardening response of approximately 706 MPa. This value is more than double the age-hardening response of the 0Cu steel in the peak-aged condition (~304 MPa), which indicates that Cu additions not only accelerate the age-hardening kinetics but also considerably enhance the age-hardening response. Moreover, the 1.5Cu steel with a yield strength of 1404 ± 10 MPa exhibits an elongation-to-failure of more than 10% and a reduction in area of approximately 40%. Thus, the 1.5Cu steel exhibits an excellent combination of high strength and ductility.

4. Discussion

The aforementioned results indicate that Cu additions play a crucial role in suppressing the DP reaction and promoting the CP reaction of NiAl-strengthened steels, leading to a substantial improvement in the mechanical properties. The DP and CP reactions are two competitive processes, whose combination determines the final precipitate microstructure. Therefore, in the following sections, the mechanisms for the DP reaction in Fe-Ni-Al steels will be briefly analyzed, and the underlying mechanisms for the Cu-induced CP promotion and DP suppression as well as their influence on the mechanical properties of NiAl-strengthened steels will be discussed.

4.1 Mechanisms for the DP reaction in Fe-Ni-Al steels

The classical DP reaction is of the form of $\alpha' \rightarrow \alpha + \beta$, where a single phase supersaturated α' matrix transforms behind a moving grain boundary to a more thermodynamically stable α matrix and β precipitates. The migrating grain boundary, also called reaction front, acts as a short circuit path for the diffusion of solute atoms, and the concentration difference of solutes across the migrating grain boundary provides the chemical driving force for the DP growth. Similar as eutectoid transformations in which the cooperative growth of a solute rich and solute lean phase side by side results in a lamellar or rod-like morphology, the DP reaction leads to the formation of periodic arrays of NiAl rods in the Fe-Ni-Al steels. In addition, the formation of both DP and CP regions was observed in all the aging conditions studied, and the area fraction of DP regions increases with aging time (confer Fig.

1). These observations indicate that the DP reaction proceeds frontally by sweeping the CP regions. Thus, the DP reaction in the Fe-Ni-Al steels can be sketched in Fig. S3 and described by

$$\alpha' + NiAl_{CP} \rightarrow \alpha + NiAl_{DP} \tag{1}$$

where $NiAl_{CP}$ and $NiAl_{DP}$ are NiAl precipitates in the CP and DP regions, respectively, and the supersaturation of α' changes with aging time because the CP reaction continuously consumes the supersaturated matrix. Therefore, the competition between the DP and CP reactions determines the microstructural morphology of the Fe-Ni-Al steels.

4.2 Mechanisms for Cu-induced CP acceleration and its influence on DP suppression

The 1.5Cu steel has higher number densities and volume fractions of CP nanoparticles than the 0Cu steel in the early stage of precipitation, which indicates that Cu additions play a crucial role in accelerating the CP reaction. APT reveals that the accelerated CP of the 1.5Cu steel is associated with the nanoscale partitioning of Cu atoms to the NiAl nanoparticles. To understand the atomistic mechanism of how the Cu partitioning affects the NiAl precipitation, we performed the first-principles calculations for investigating the interaction of Cu with Ni−Al pairs. Fundamentally, the attractive interaction of Ni−Al pairs provides a chemical driving force for NiAl precipitation. The influence of Cu atoms on the formation energy of Ni−Al pairs was calculated. To consider the influence of the number of Ni−Al pairs in the calculation, we constructed three 128-atom supercells comprising one, two, and three Ni−Al pairs on the basis of a bcc−Fe lattice, in which Ni and Al atoms have the first nearest-neighbor relationship. To study the interaction of Cu with the Ni−Al pairs, for each case, one Fe atom nearby the Ni−Al pair was substituted by one Cu atom. The formation energies of the Ni−Al pair in the Cu-free ($E_{Cu\text{-}free}$) and Cu-containing ($E_{Cu\text{-}containing}$) supercells were calculated using the following equations:

$$E_{Cu-free} = \left[E_{(128-2n)Fe\text{-}nNi\text{-}nAl} + (2n\text{-}1)E_{128Fe}\right] \text{-} (nE_{127Fe\text{-}1Ni} + nE_{127Fe\text{-}1Al}) \quad (2)$$

$$E_{Cu-containing} = \left[E_{(127-2n)Fe\text{-}nNi\text{-}nAl\text{-}1Cu} + 2nE_{128Fe}\right] \text{-} (nE_{127Fe\text{-}1Ni} + nE_{127Fe\text{-}1Al} + E_{127Fe-1Cu}) \quad (3)$$

where E with different composition subscripts represents the total energies of the 128-atom supercells with various Fe, Ni, Al, and Cu lattice occupancies, and $n = 1, 2, 3$ represents the number of Ni−Al pairs. The calculated values of $E_{cu\text{-}free}$ and $E_{Cu\text{-}containing}$ are presented in Fig. 10. In all the three cases, the formation energy of Ni−Al pairs in the Cu-containing supercells are lower than that of Ni−Al pairs in the Cu-free supercells, which indicates that Cu enhances the attractive interaction of the Ni−Al pairs and thereby increases the chemical driving force for NiAl precipitation. Thus, the Cu additions accelerate the NiAl precipitation, leading to a high number density and volume fraction of CP nanoparticles in the 1.5Cu steel (confer Fig. 6).

Because the CP and DP reactions are two competitive processes to lower the total free energy by consuming the supersaturated solid-solution matrix, the accelerated CP induced by Cu partitioning would inevitably affect the DP reaction. Fundamentally, the DP reaction involves the cellular growth of alternating lamellae of NiAl precipitates and α-Fe matrix (with greatly reduced supersaturation) behind a moving grain boundary, ahead of which is the untransformed or continuously transformed matrix with a high supersaturation [27-29]. The concentration difference of solutes (here Ni and Al) across the migrating grain boundary functions as a chemical driving force for DP growth. The evolutions of Ni and Al in the CP matrix of the 0Cu and 1.5Cu steels are illustrated in Figs. 11a and b, respectively, as a function of aging time. In the 0Cu steel, the Al concentration of the CP matrix exhibits a slow and gradual decrease with the aging time, decreasing from approximately 4 at.% in the 7.5-min aged condition to approximately 3.2 at.% in the 30-min aged condition and to approximately 1.9 at.% in the 2-h aged condition. Compared with the 0Cu steel, the 1.5Cu steel exhibits a considerably more rapid decrease in the Al concentration of the CP matrix, decreasing drastically from approximately 4 at.% in the as-quenched condition to approximately 2.9 at.% in the 7.5-min aged condition, 1.9 at.% in the 30-min aged condition, and 1.4 at.% in the 2-h aged condition. A similar trend was observed for the Ni concentration in the CP matrix of the two steels. These observations indicate that the CP reaction of the 1.5Cu steel consumes the supersaturated matrix more rapidly than that of the 0Cu steel, which leads to a substantial decrease in the Ni and Al supersaturations in the early stages of precipitation. According to Petermann and Hornbogen [43], the chemical driving force for the DP reaction can be described by:

$$\Delta G_{DP} = \text{-}RT[x^{Fe}\ln\frac{x^{Fe}}{x_e^{Fe}} + x^{Ni}\ln\frac{x^{Ni}}{x_e^{Ni}} + x^{Al}\ln\frac{x^{Al}}{x_e^{Al}} + x^{Cu}\ln\frac{x^{Cu}}{x_e^{Cu}}] \tag{4}$$

Where R is the gas constant, T is the temperature, x^{Fe}, x^{Ni}, x^{Al}, and x^{Cu} are the Fe, Ni, Al, and Cu concentrations in the CP matrix, respectively, x_e^{Fe}, x_e^{Ni} and x_e^{Al} are the Fe, Ni, and Al concentrations in the DP matrix, respectively, and x_e^{Cu} is estimated from the Cu concentration in the 1.5Cu steel matrix in the 2-h aged condition. With the input of APT concentrations in the different conditions, the chemical driving force for the DP reaction was estimated and is presented in Fig. 11c. For the 0Cu steel, the free energy of the DP reaction was estimated to be −151 ± 8 J/mol in the 7.5-min aged condition and −98 ± 10 J/mol in the 30-min aged condition, indicating a high chemical driving force for the growth of DP cells. By contrast, the free energy for the DP reaction in the 1.5Cu steel is −90 ± 12 J/mol in the 7.5-min aged condition, which is considerably higher than that in the 0Cu steel under the same condition. Moreover, the free energy for the DP reaction of the 1.5Cu steel is close to zero in the 30-min and 2-h aged conditions. Therefore, the chemical driving force for the DP growth is drastically reduced because of CP acceleration, which contributes to the suppression of DP reactions in the 1.5Cu steel.

4.3 Effects of grain boundary Cu segregation on DP suppression

We now analyze the effect of Cu segregation at grain boundaries on the DP reaction of the NiAl-strengthened steels. APT reveals that the grain boundary segregation of Cu, Ni, and C in the NiAl-strengthened steels occurs at an early stage of aging, which can influence the grain boundaries energy of the steels. The change of the grain boundary energy due to the grain boundary segregation can be described by [44]:

$$\Delta G = \Gamma(\Delta H_{seg} - T\Delta S_{seg}) \tag{5}$$

where ΔG is the change in the grain boundary energy caused by solute segregation, Γ is the additional solute at the grain boundary, T is the temperature, and ΔH_{seg} and ΔS_{seg} are the enthalpy and entropy changes associated with segregation of solutes from the matrix to grain boundaries, respectively. The entropy term contains two components: one is the loss of configurational entropy of the matrix, and the other is the increase of grain boundary interfacial entropy. The calculation of net change of entropy in multicomponent alloys is very complicated, and it is generally considered that the enthalpy term plays a more important role than the entropy term. Thus, the entropy term is often ignored for simplified analyses in the literature [45-48]. Here, we follow this approach and estimate the contribution of segregation-induced enthalpy change to the grain boundary energy. ΔH_{seg} can be estimated using the McLean isotherm [49]:

$$\frac{X_{gb}}{1-X_{gb}} = \frac{X_{gi}}{1-X_{gi}}\exp(\frac{\Delta H_{seg}}{RT}) \tag{6}$$

where X_{gb} and X_{gi} are the mole fractions of solutes at the grain boundary and grain interior, respectively, R is the gas constant, and T is the temperature. With the inputs of $X_{gb,Cu}$ = 4.0 at.%, $X_{gb,Ni}$ = 9.8 at.%, $X_{gb,C}$ = 0.8 at.%, $X_{gi,Cu}$ = 1.0 at.%, $X_{gi,Ni}$ = 7.3 at.%, $X_{gi,C}$ = 0.05 at.%, Γ_{Cu} = 3 atom/nm^2, Γ_{Ni} = 2.5 atom/nm^2, Γ_C = 0.3 atom/nm^2, R = 8.31 J/K·mol, and T = 823 K, the decrease in the grain boundary energy due to Cu segregation is calculated to be 0.05 J/m^2, which accounts for 4%−17% of the total grain boundary energy in bcc steels (0.3−1.5 J/m^2) [50,51]. Similarly, the reduction of grain boundary energy due to Ni and C segregation are estimated to be both approximately 0.01 J/m^2, which is much smaller than that due to Cu segregation (0.05 J/m^2), indicating that Cu plays a dominant role in decreasing the grain boundary energy. According to the Fournelle and Clark's mechanism [52,53] the nucleation rate of DP can be described by

$$I_{DP} \propto v \exp[-\frac{E}{RT}] \frac{\gamma V_m}{d} P_{nuc} \tag{7}$$

where v is the vibration frequency of the grain boundary considered as a membrane, E is the activation energy for the vibration of the grain boundary, R is the gas constant, T is the temperature, γ is the grain boundary energy, V_m is the molar volume, d is the grain size, and P_{nuc} is the probability that the displacement of the grain boundary induced by capillarity forces allows a DP nodule to nucleate. From Eq. (7), the nucleation rate of DP shows a positive correlation with the grain boundary energy. Thus, the Cu-induced reduction of grain boundary energy is likely to decrease the nucleation rate of DP, thereby contributing to the suppression of DP reactions in the Cu-containing steels. A similar phenomenon was observed in a U-10Mo (wt.%) alloy, where the grain boundary segregation of Si, Al, Mn, and Ni was reported to inhibit the DP nucleation [54].

On the basis of the aforementioned discussion in **Sections 4.2** and **4.3**, the mechanisms for the effect of Cu partitioning on the DP reaction can be twofold; the major effect should be due to the Cu-induced acceleration of the CP reaction, which significantly reduces the chemical driving force for the DP growth, while the minor effect is possibly due to the Cu-induced reduction of grain boundary energy, which is likely to decrease the nucleation rate of DP reaction. The effects of Cu on the CP and DP behaviors of the NiAl-strengthened steels is summarized in the following text and schematically illustrated in Fig. 12. In the Cu-free steels, DP rods form at the grain boundaries, whereas CP nanoparticles form in the grain interiors. The CP nanoparticles and DP rods grow as the precipitation progresses, which leads to a mixed microstructure containing both CP and DP regions. By contrast, Cu additions play a crucial role in not only promoting the CP formation but also in suppressing the DP reaction, resulting in the uniform precipitation of CP nanoparticles with high number densities throughout the matrix.

4.4 Effects of Cu on the NiAl precipitation strengthening mechanism

The mechanical results reveal that Cu additions considerably enhance the strength of the NiAl-strengthened steels (Fig. 9), which is accompanied with a slight decrease in the grain size and a drastic change in the precipitate microstructure, including the precipitate size, volume fraction, and distribution. The contribution of the grain size refinement by the 1.5Cu addition was estimated to be 78 MPa (see Supplementary Material), which is not significant compared to age hardening. To gain a basic understanding of the composition–microstructure–mechanical property relationship in the NiAl-strengthened steels, the strengthening mechanisms of the NiAl precipitates were modeled.

The interactions between NiAl nanoparticles and dislocations occur either by Orowan dislocation looping or particle shearing. The increase in yield strength by the Orowan dislocation looping mechanism is given by [55]

$$\Delta\sigma_{Orowan} = 0.84M\left(\frac{1.2Gb}{2\pi L}\right)\ln\left(\frac{\lambda}{2b}\right) \tag{8}$$

where $M = 3$ is the Taylor factor, $G = 80$ GPa is the shear modulus of the α-Fe matrix, $b = 0.25$ nm is the Burgers Vector [56], $\lambda = 2(2/3)^{1/2}r$ is the outer cut off distance, and $L = 0.866/(rN)^{1/2}$ is the mean interparticle spacing [56], where r and N are particle radius and number density, respectively. Using the experimental data of particle radii and number densities, the strengthening contributions from the Orowan dislocation looping mechanism is determined to be approximately1151 MPa for the 0Cu steel and approximately 1157 MPa for the 1.5Cu steel. These values are considerably higher than the experimental values of yield strength increments, implying that the Orowan bypass mechanism might not be operative in the currently studied steels.

Strengthening by particle shearing occurs primarily due to order strengthening ($\Delta\sigma_{order}$), modulus strengthening ($\Delta\sigma_{modulus}$), and coherency strengthening ($\Delta\sigma_{coherency}$) [57]. The equations for these contributions are expressed by [57]:

$$\Delta\sigma_{order} = 0.81M\frac{\gamma_{apb}}{2b}\left[\left(\frac{3\pi f}{8}\right)^{1/2}\right] \tag{9}$$

$$\Delta\sigma_{modulus} = \frac{M\Delta G}{4\pi^2}\left(\frac{3\Delta G}{Gb}\right)^{1/2}\left[0.8-0.143\ln\left(\frac{r}{b}\right)\right]^{2/3} r^{1/2} f^{1/2} \tag{10}$$

$$\Delta\sigma_{coherency} = 4.1MG\varepsilon^{3/2} f^{1/2}\left(\frac{r}{b}\right)^{1/2} \tag{11}$$

where the parameters of M, G, and b are the same as those in Eq. (8), $\Delta G = 7$ GPa is the difference between the shear modulus of the matrix (80 GPa) and NiAl phase (73 GPa) [58], $f = 4/3\pi r^3 N$ is the volume fraction of the NiAl nanoparticles, $\gamma_{apb} = 0.5\ \mathrm{J{\cdot}m^{-2}}$ is the average value of the anti-phase energy of B2-NiAl from literature [59,60], and $\varepsilon = 2/3(\Delta a/a)$ is the constrained lattice mismatch between the NiAl precipitates and matrix (the constraint of the matrix reduces the free expansion of the precipitates by a factor of 2/3; see Supplementary Material) [56]. Using experimental data on the particle radii and volume fractions, the strengthening contributions of CP nanoparticles in the 0Cu and 1.5Cu steels in the 2-h aged condition were estimated. These results are summarized in Table 4. As suggested in Ref. 61, the increment in strength due to particle shearing is taken as the larger value between $\Delta\sigma_{order}$

and ($\Delta\sigma_{modulus}$ + $\Delta\sigma_{coherency}$) because $\Delta\sigma_{order}$ contributes to strengthening during the shearing process and ($\Delta\sigma_{modulus}$ + $\Delta\sigma_{coherency}$) contributes to strengthening before shearing. As listed in Table 4, the increments of order strengthening are considerably larger than the sum of coherency and modulus strengthening, which implies that order strengthening is the operative mode for NiAl precipitation strengthening. For the 1.5Cu steel with a uniform distribution of CP nanoparticles, the calculated strengthening response is approximately 663 MPa in the 2-h aged condition, which is close to our experimental value (706 MPa) under the same condition. For the 0Cu alloy with a mixture of CP (30%) and DP (70%) regions, the strength increment from the CP nanoparticles is estimated as 166 MPa in the 2-h aged condition, whereas that from the DP rods (138 MPa) is back-calculated by subtracting CP strengthening from the total strengthening determined experimentally. Although the DP region occupies a high area fraction (70%) of the microstructure in the 0Cu steel, its strengthening contribution is relatively small because of the coarseness of the DP rods. By contrast, the high number densities of CP nanoparticles contribute to a high degree of precipitation strengthening. Therefore, in addition to the fundamental understanding of the precipitation mechanism, suppression of the DP reaction of the NiAl-strengthened steels through Cu partitioning is also technologically significant.

5. Summary

In this study, we proved that Cu effectively suppresses the coarse-sized discontinuous NiAl precipitation along grain boundaries and promotes the nano-sized continuous NiAl precipitation in grain interiors, which leads to a twofold enhancement in strengthening in the ferritic Fe−Cu−Ni−Al steels. The following conclusions are drawn according to the systematic investigations of the precipitate microstructural evolutions, precipitation thermodynamics and kinetics, grain boundary segregations, and mechanical properties of the NiAl-strengthened steels with and without Cu additions:

1. NiAl precipitation in ferritic steels occurs in two modes, namely forming nano-sized CP particles and coarse-sized DP rods. In the 0Cu steel, the microstructure consists of a mixture of coarse-sized DP rods along grain boundaries and nano-sized CP particles in the grain interiors. With an appropriate amount of Cu (1.5 wt.%), the formation of coarse-sized DP rods is completely suppressed, which results in the uniform precipitation of NiAl nanoparticles throughout the matrix.
2. The suppression of the DP reaction is attributed mainly to the acceleration of CP reaction through Cu partitioning to NiAl precipitates, which decreases the chemical driving force for the DP growth through a fast reduction of supersaturation. First-principles calculations reveal that Cu enhances the interaction of Ni-Al pairs and promotes the NiAl precipitation, which leads to the accelerated precipitation of NiAl nanoparticles.
3. APT reveals that Cu segregates at the grain boundaries of the Fe−Cu−Ni−Al steels in the early stage of aging, which reduces the grain boundary energy. According to the Fournelle and Clark's mechanism, the Cu-induced reduction of grain boundary energy is likely to decrease the nucleation rate of DP, thereby contributing to the suppression of DP reactions in the Cu-containing steels. This is the minor effect of Cu partitioning on suppressing the DP reaction of the NiAl-strengthened steels.
4. Cu additions considerably enhance the strengthening response of NiAl precipitates in ferritic steels, which leads to the development of new NiAl-strengthened steels with a good combination of high yield strength (1400 MPa) and good ductility (10%). Strengthening modelling indicates that the CP nanoparticles exhibit a more effective strengthening effect than the coarse-sized DP rods in the NiAl-strengthened steels.

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Figure captions

Fig. 1. Microstructures of the 0Cu steel in the different conditions: (a) as-quenched, (b) 7.5 min at 550 °C, (c) 30 min at 550 °C, and (d) 2 h at 550 °C. (e) SAED pattern and (f) DF-TEM image of the DP region of the 0Cu steel in the 2-h aged condition.

Fig. 2. APT atom maps, 25%(Ni + Al) isoconcentration surfaces, and proximity histograms of DP regions in the 0Cu steel: (a) 7.5 min at 550 °C, (b) 30 min at 550 °C, and (c) 2 h at 550 °C.

Fig. 3. Microstructures of the Cu-containing steels in the different conditions: (a) 0.5Cu, 7.5 min at 550 °C, (b) 0.5Cu, 30 min at 550 °C, (c) 0.5Cu, 2 h at 550 °C, (d) 1Cu, 7.5 min at 550 °C, (e) 1Cu, 30 min at 550 °C, (f) 1Cu, 2 h at 550 °C, (g) 1.5Cu, 7.5 min at 550 °C, (h) 1.5Cu, 30 min at 550 °C, and (i) 1.5Cu, 2 h at 550 °C.

Fig. 4. Area fractions of DP regions of the 0Cu, 0.5Cu, 1Cu, and 1.5Cu steels as a function of aging time.

Fig. 5. CP nanoparticles of 0Cu and 1.5Cu steels in the different aging conditions: (a) 0Cu, 7.5 min at 550 °C, (b) 0Cu, 30 min at 550 °C, (c) 0Cu, 2 h at 550 °C, (d) 1.5Cu, 7.5 min at 550 °C, (e) 1.5Cu, 30 min at 550 °C, (f) 1.5Cu, 2 h at 550 °C.

Fig. 6. (a) Particle radii and (b) volume fractions of CP nanoparticles of the 0Cu and 1.5Cu steels as a function of aging time.

Fig. 7. Proximity histograms of CP nanoparticles of the 0Cu and 1.5Cu steels in the different aging conditions: (a) 0Cu, 7.5 min at 550 °C, (b) 1.5Cu, 7.5 min at 550 °C, (c) 0Cu, 30 min at 550 °C, (d) 1.5Cu, 30 min at 550 °C, (e) 0Cu, 2 h at 550 °C, and (f) 1.5Cu, 2 h at 550 °C. The insets show the 1-nm-thick atom maps through representative nanoparticles showing the distributions of Ni (green), Al (cyan), and Cu (red) atoms.

Fig. 8. Grain boundary microstructures of the 1.5Cu steel in the different conditions: (a) atom maps of C, Cu, Ni, and Al in the 1-min aged condition, and (b) atom maps of C, Cu, Ni, and Al, 25%(Ni + Al) isoconcentration surfaces, and proximity histogram of grain boundary precipitates in the 2-h aged condition.

Fig. 9. Mechanical properties of the 0Cu and 1.5Cu steels: (a) Vickers microhardness of the steels as a function of aging time at 550 °C, and (b) stress-strain curves of the steels in the as-quenched and 2-h aged conditions.

Fig. 10. First-principles calculations of the formation energies of Ni-Al pairs in the Cu-free and Cu-containing supercells. The compositions of the six supercells are $Fe_{126}Ni_1Al_1$, $Fe_{125}Ni_1Al_1Cu_1$, $Fe_{124}Ni_2Al_2$, $Fe_{123}Ni_1Al_1Cu_1$, $Fe_{122}Ni_3Al_3$, and $Fe_{121}Ni_3Al_3Cu_1$.

Fig. 11. (a) Ni and (b) Al concentrations in the matrix of CP and DP regions in the 0Cu and 1.5Cu steels as a function of aging time, and (c) the chemical driving force for the DP growth.

Fig. 12. Schematics showing the precipitation mechanism of NiAl-strengthened steels with and without Cu.