**Precipitation mechanism and mechanical properties of an ultra-high strength steel
hardened by nanoscale NiAl and Cu particles**

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Abstract

We report on the alloy design strategies, precipitation mechanism and mechanical properties of an ultra-high strength steel hardened by co-precipitation of nanoscale NiAl and Cu particles. The steel, developed through a computational-aided alloy design approach, exhibits a tensile strength of ~1.9 GPa, an elongation of ~10% and a reduction in area of ~40%. Atom probe tomography reveals an interesting type of co-precipitation mechanism of NiAl and Cu nanoparticles, in which the NiAl particles first come out of the supersaturated solid solution and the rejection of Cu solutes leads to the heterogeneous precipitation of Cu particles adjacent to the NiAl particles. The observed precipitation sequence of “supersaturated solid solution → NiAl → NiAl + Cu” is substantially different from the one previously reported in Cu-strengthened steels, which involves the process of “supersaturated solid solution → Cu → Cu + NiAl”. The modulation of the precipitation sequence is attributed not only to the relatively high Ni/Cu and Al/Cu ratios but also the synergistic combination of Ni, Al, Mn and Cu additions in the steel. In

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addition, APT also reveals the precipitation of a small amount of nanoscale $\text{Fe}_3(\text{Mo,W})_3\text{C}$ - and NbC-type carbides. The combination of the strengthening effects from the nanoscale NiAl particles, Cu particles and carbides contributes significantly to the overall ultra-high strength of the steel.

Keywords: NiAl and Cu co-precipitate; precipitation; mechanical property; structure-property relationship; atom probe tomography

1. Introduction

Ultra-high strength steels are becoming increasingly important in aerospace, power generation, shipbuilding, and automotive industries. Basically, the strengthening of steels 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 to increase the tensile and/or creep strength of steels [2-7]. The degree of strengthening so obtained is highly dependent upon the type, number density, size and spatial distribution of the particles, and also the nature of the interaction of the dislocations with the particles [1]. Among the various types of potential nanoparticles to be considered for precipitation hardening in steels, Cu and NiAl nanoparticles constitute two classes of effective strengthening phases, allowing the development of low-carbon steels with a good combination of high strength, high ductility and good weldability [8-14].

Recently, the co-precipitation of nanoscale Cu and NiAl particles in high strength steels has attracted considerable attentions, which offer a promising way to effectively strengthen the steels without a significant reduction in ductility [15-18]. Previous work was focused mainly on the Fe-Cu-Ni-Al-based steels with relatively low Ni/Cu and Al/Cu ratios, in which Cu nanoparticles are the dominant strengthening phase and NiAl nanoparticles provide a supplement strengthening effect. Regarding to the precipitation mechanism, it is generally accepted that coherent body-centered cubic (bcc) Cu nanoparticles nucleate first from the supersaturated solid solution, and Ni and Al tend to segregate at the interface between the Cu nanoparticles and α -Fe matrix [16,19-21]. The interfacial segregation of Ni and Al leads to the heterogeneous precipitation of NiAl adjacent to the Cu nanoparticles, thereby forming composite nanoparticles

[22-26]. It is known that small variations in the Ni, Al and Cu contents can lead to sensitive differences in the precipitation characteristics, including the composition, size and number density of the Cu and NiAl nanoparticles, thereby significantly influencing the degree of strengthening. Since NiAl, a highly stable B2-ordered intermetallic phase [27-29], is much harder than Cu, it can provide more efficient strengthening effects in steels. Therefore, it is interesting to further tune the Ni/Cu and Al/Cu ratios to properly enhance the precipitation of NiAl. To date, however, investigations on Cu- and NiAl-strengthened steels with relatively high Ni/Cu and Al/Cu ratios are limited, and the corresponding precipitation mechanism remains elusive. Therefore, it is of both fundamental and technological importance to obtain detailed knowledge on the precipitation mechanism of the steels with relatively high Ni/Cu and Al/Cu ratios, so that the precipitation reaction may be controlled to achieve optimal properties.

The purposes of this work are twofold. First, to obtain a fundamental understanding of the co-precipitation mechanism of nanoscale NiAl and Cu particles in the steels with relative high Ni/Cu and Al/Cu ratios. Second, to develop new ultra-high strength steel by reasonably combining the strengthening effects of nanoscale NiAl and Cu particles as well as a small amount nanoscale carbides. In this work, a computational-aided alloy design approach was employed to guide the alloy design, and the precipitation nanostructural features and mechanical properties of the prototype steel were carefully characterized by experimental studies. Since the Cu and NiAl nanoparticles usually have a coherent relation to the magnetic Fe-based matrix, it is difficult to quantitatively characterize the morphology and composition of these nanoparticles, particularly in the early stages of precipitation, using conventional transmission electron microscope (TEM) because of a weak diffraction and phase contrast [16]. Atom probe tomography (APT) is an alternative high-resolution characterization method, which provides

three-dimensional (3D) elemental mapping with nearly atomic resolution and gives information on the topology of interfaces and local chemical gradients [30-32]. In this work, the size, number density, composition, particle configuration and spatial distribution of the NiAl and Cu nanoparticles as a function of aging time were systematically characterized by APT. Particular attention was paid to the mechanistic understanding of the co-precipitation mechanism in the steel with relatively high Ni/Cu and Al/Cu ratios.

2. Computational-aided alloy design

Thermodynamic calculations offer an effective means by which the phase relationship in multi-component alloys can be readily predicted [33,34]. In this study, the Thermo-Calc 3.0.1 software with Fe database (TCFE7), a unique thermodynamic program for calculating phase constitutions and transformations in Fe-based multi-component alloys, is employed to provide guidelines for alloy design of the high-strength steel hardened by NiAl and Cu nanoparticles as well as a small amount of carbides. Each step of the alloy design procedure will be presented below.

First, the carbon content of the steel is set based on the consideration of both weldability and carbide hardening. Carbon is known as one of the most important alloying elements affecting the steel weldability, and high-carbon steels tend to suffer from solidification cracking in the welds [35]. Similar to the carbon level in the weldable, high-strength steels Navy HSLA-80 and HSLA-100 [8], a low carbon content of 0.05 wt.% is set for high weldability. Moreover, to prevent the formation of cementite and to ensure good ductility, strong carbide-forming elements, including Nb, Mo and W, are introduced into the steel. As suggested by commercial precipitation-hardening martensitic steels [36], a combination of 0.07 wt.% Nb together with Mo

and W is added to form nanoscale alloy carbides. In addition, boron has been found to improve the ductility of high-strength alloys by enhancing their grain-boundary cohesion and suppressing the intergranular fracture [37-39]. To achieve a good strength-ductility combination, the boron content is set to be 0.01 wt.% in the steel.

Second, Cu precipitation characteristics are strongly dependent on the Cu supersaturation and aging condition used. A solutionizing treatment at 900 °C and an aging treatment at 550 °C are initially chosen based on the previous studies for optimizing the particle and grain sizes in Cu- and NiAl-strengthened steels [26,40]. The fraction of the Cu phase as a function of Cu content and heat-treatment temperature is calculated by Thermo-Calc, as shown in Fig. 1a. At 550 °C, less than 0.2 wt.% Cu would be completely dissolved in the α -Fe solid solution, while at 900 °C, the Cu phase starts to precipitate out when the Cu content is greater than 3.5 wt.%. Therefore, the Cu level should be within the range of 0.2-3.5 wt.%. Previous studies also suggest that the Cu content should be at least 1.0 wt.% for significant strengthening [8-10,22-26]. On the other hand, Cu has a low melting point compared to the α -Fe matrix, and excessive Cu additions tend to cause a hot cracking phenomenon known as “hot shortness” [41]. Based on these considerations, the Cu content in the steel is set to be 1.5 wt.%.

Finally, the content of Ni, Al and Mn are optimized to promote the formation of NiAl-type nanoparticles while minimizing the formation of undesired phases including retained austenite and δ -ferrite. It is noted that Ni, an austenite stabilizer, encourages the formation of retained austenite, while too much Al would lead to the retention of δ -ferrite. It was reported that 15% retained austenite in precipitation hardened steels would not significantly degrade the strength [42], while even a small fraction of δ -ferrite seriously worsened the toughness [43]. Thus, an upper limit of 15% for retained austenite and zero tolerance for δ -ferrite are set in the

steel. To predict the allowable Ni and Al contents, the fraction of retained austenite and δ -ferrite as a function of Ni and Al contents are calculated by Thermo-Calc. The isothermal sections of the Fe- x Ni- y Al-1.5Cu-1.5Mo-1.5W-0.07Nb-0.05C-0.01B system at a solutionizing temperature of 900 °C and an aging temperature of 550 °C are illustrated in Fig. 1b and c, respectively. The fraction of δ -ferrite at 900 °C increases with increasing Al contents and decreasing Ni contents, whereas that of retained austenite at 550 °C behaves in the opposite way. The composition range fulfilling the requirements for both retained austenite and δ -ferrite is shown in Fig. 1d. The composition with 8 wt.% Ni and 2 wt.% Al (indicated by the black dot) is close to the maximum alloying level. Considering the stoichiometry of the NiAl intermetallic compound, 5 wt.% Ni is enough for fixing 2 wt.% Al. The remaining Ni can be substituted by ~3 wt.% Mn, since Mn has a similar effect on retarding the formation of δ -ferrite as Ni. In addition, Mn plays an important role in enhancing the nanoscale precipitation of NiAl by partially substituting for Al [44]. More importantly, the substitution of Mn for Ni significantly lowers the material cost, which is in line with the design of cost-effective steels. Based on all above design guidance, the final optimal composition is derived as Fe-5Ni-2Al-3Mn-1.5Cu-1.5Mo-1.5W-0.07Nb-0.05C-0.01B (wt.%).

3. Experimental

Alloy ingots were prepared by arc-melting a mixture of the constituent elements with purity better than 99.9 wt.% in a Ti-gettered high-purity argon atmosphere. Repeated melting was carried out at least five times to ensure the chemical homogeneity. The melted alloys were then drop-cast into a copper mold with dimensions of 15 × 30 × 100 mm. The resulting plates were successfully cold rolled without difficulties by multiple passes with a total reduction of ~66%

and solution-treated for 30 min at 900 °C, followed by water quenching, and then aged isothermally at 400 to 550 °C for various periods of time up to 128 h.

Sections of the heat-treated samples perpendicular to the rolling direction were polished to a final surface finish of 0.05 μm using standard mechanical polishing procedures. Hardness measurements were conducted on polished surface of the samples using 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} . Fracture surfaces were examined by scanning electron microscopy (SEM).

Thin TEM foils were prepared with care for a large electron transparent area and minimum magnetic influence. 3-mm-diameter discs were thinned to electron transparent by a twin-jet electrochemical polisher at 35 V in a 5 vol.% HClO_4 methanol electrolyte at a low temperature. The thin foils were then gently ion milled to remove surface contamination. TEM characterization was conducted using a JEOL 2100F microscope operated at 200 kV.

The needle-shaped specimens required for APT were fabricated by a combination of standard electropolishing methods followed by annular milling in a FEI Nova 200 focused ion beam/scanning electron microscope (FIB/SEM) [30]. The APT characterizations were performed in a CAMECA Instruments LEAP 4000X HR local electrode atom probe. The specimens 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 (IVAS) version 3.6.6 was used for 3D reconstructions, composition analysis and the creation of isoconcentration surfaces.

4. Results

4.1 Mechanical properties

Hardness measurements were conducted to evaluate the age hardening response of the steel. The Vickers hardness of the specimens aged for up to 128 h at 400 to 550 °C is shown in Fig. 2. The steel shows a hardness of ~440 HV in the as-quenched condition. At aging temperatures of 400 and 450 °C, no hardness peaks appear within the 128 h aging period, indicating that the age hardening kinetics is very slow at these temperatures. Upon aging at 500 °C, the hardness increases gradually to ~615 HV after aging for 8 h, and prolonged aging leads to the decrease of the hardness due to an over-aging effect. During aging at 550 °C, the steel shows a similar trend in hardness as that at 500 °C but at a relative fast rate of age hardening, reaching the peak hardness of ~620 HV at 2 h, resulting in a pronounced increase in hardness (~180 HV) as compared with the as-quenched sample. The above results indicate that the aging treatment at 550 °C provides an appropriate condition for obtaining a substantial age hardening response within a reasonable period of time.

Room-temperature tensile tests were performed to further investigate the mechanical behavior of the steel in the peak hardening condition (aging at 550 °C for 2 h). The engineering stress-strain curve of the steel is shown in Fig. 3, and the corresponding fracture surfaces are shown in the insets. The steel exhibits an ultimate tensile strength of ~1.9 GPa, an elongation-to-failure of ~10% and a reduction in area of ~40%, indicating a good combination of ultra-high strength and good ductility. In addition, obvious necking and large reductions in area are clearly

observed from the fractured samples. The fracture surface shows a micro-void coalescence fracture mode with a lot of fine dimples, indicating a characteristic mode of a ductile fracture.

It is expected that the mechanical properties can be further optimized by optimizing the alloy composition and heat-treatment parameters, which merits a systematical investigation in the future. In the subsequent sections, we will focus our efforts on the mechanistic understanding of the nanoscale precipitation and properties of the ultra-high strength steel.

4.2 APT and TEM characterization

4.2.1 Characterization of nanoscale carbides

The microstructure of nanoscale carbides in the specimen aged for 2 h at 550 °C were characterized by TEM. Two categories of spheroidal nanoscale carbides are observed, as shown in Fig. 4a, one category with an average diameter of ~40 nm and the other category of ~10 nm. The energy dispersive spectroscopy (EDS) spectrums of the two categories of nanoscale carbides are presented in Fig. 4b. The EDS analysis reveals that the coarser carbides are enriched in Mo and W, whereas the finer ones are enriched in Nb. High-resolution TEM image of a representative Mo/W-enriched carbide and its corresponding fast Fourier transformation (FFT) pattern are presented in the insets in Fig. 4a. The FFT pattern together with the EDS spectrum indicates that the coarser carbides are of $\text{Fe}_3\text{Mo}_3\text{C}$ -type.

Moreover, the Mo/W-enriched and Nb-enriched carbides are also detected by APT. One advantage of APT over other nanoanalytical techniques is the quantitative detection of all elements with a super-high sensitivity, including the light-element carbon for which concentration is not readily quantified by TEM/EDS analysis, in particular when the nanoscale features of interest are smaller than the TEM foil thickness [30-32]. The APT compositions of

the two types of nano-carbides, as estimated from the deconvolution of the peaks in the mass spectra of ions collected from the interior of the particles, are given in Table 1. The atomic ratio of Fe:(Mo+W):C in the coarser carbides is approximately 3:3:1, which is in accordance to that of $\text{Fe}_3(\text{Mo,W})_3\text{C}$ -type carbides and in agreement with the TEM results. The atomic ratio of (Nb+Mo+W):C in the finer carbides is close to ~ 1 , suggesting these finer carbides are of NbC-type with certain amounts of Mo and W substitutional for partial Nb.

4.2.2 Nanoscale co-precipitation of NiAl and Cu particles

We now characterize the detailed precipitation evolution of the nanoscale NiAl and Cu particles, the primary strengthening phases in the steel. The 25% (Ni+Al) concentration and 5% Cu concentration isosurfaces are used to visualize the NiAl and Cu nanoparticles, respectively. The nanostructures of the two types of particles in the specimens after aging for 0.5, 2, 8 and 128 h at 550 °C are shown in Fig. 5a, b, c and d, respectively. High number densities of spheroidal NiAl and Cu nanoparticles are detected readily in the 0.5-8 h aged specimens, and both types of particles tend to coarsen with aging time. In the 128 h condition, a Cu particle in close contact with a NiAl particle is observed, but both particles are too coarse for quantitative analysis of sizes and number densities. Nevertheless, the compositions in this long-term aged condition can be analyzed, which is helpful in gaining an insight into the compositional evolution of the nanoparticles.

The average radius and number density of the NiAl and Cu nanoparticles as a function of aging time are shown in Fig. 6a and b, respectively. Upon isothermal aging at 550 °C, the average radius of the NiAl particles increases continuously from $\sim 1.1 \pm 0.4$ nm at 0.5 h to $\sim 1.7 \pm 0.56$ nm at 2 h and further to $\sim 2.8 \pm 1.0$ nm at 8 h, while that of the Cu particles increases

slightly from $\sim 1.1 \pm 0.4$ nm at 0.5 h to $\sim 1.4 \pm 0.5$ nm at 2 h and further to $\sim 1.9 \pm 0.7$ nm at 8 h. Meanwhile, the number density of the NiAl nanoparticles decreases monotonically from $\sim 3.9 \times 10^{24} \text{ m}^{-3}$ at 0.5 h to $\sim 2.8 \times 10^{24} \text{ m}^{-3}$ at 2 h and further to $\sim 5.0 \times 10^{23} \text{ m}^{-3}$ at 8 h. In comparison, the variation of the Cu nanoparticles in number density is rather complex with aging time, which increases from $\sim 2.5 \times 10^{23}$ to $\sim 5.2 \times 10^{23} \text{ m}^{-3}$ as the aging time increases from 0.5 h to 2 h and then decreases to $\sim 2.2 \times 10^{23} \text{ m}^{-3}$ when the aging time further increases to 8 h. Note that the number density of the NiAl nanoparticles is more than an order of magnitude higher than that of the Cu nanoparticles in the 0.5 h condition, and the difference between the two types of nanoparticles in number density becomes smaller with aging time.

More interestingly, the relative number and location of the NiAl and Cu nanoparticles as a function of aging time can be determined by APT, and the statistical analysis of the particle configurations is illustrated in Fig. 7. In the 0.5 h condition, the $25 \text{ nm} \times 25 \text{ nm} \times 50 \text{ nm}$ volume contains 202 spheroidal NiAl particles and 13 spheroidal Cu particles. The majority of the NiAl particles are isolated particles with no Cu particles associated with them, and only $\sim 6\%$ of the NiAl particles are NiAl/Cu co-precipitates, in which the Cu particles are located on the outside surface of the NiAl particles. It is worthwhile to point that no isolated Cu particles are observed in this condition. In the 2 h condition, the $40 \text{ nm} \times 40 \text{ nm} \times 50 \text{ nm}$ volume contains 141 spheroidal NiAl particles and 32 spheroidal Cu particles. Statistical analysis indicates that $\sim 23\%$ of the NiAl particles have Cu particles associate with them and the remainders are isolated NiAl particles. In the 8 h condition, the $45 \text{ nm} \times 45 \text{ nm} \times 50 \text{ nm}$ volume contains 58 spheroidal NiAl particles and 18 spheroidal Cu particles, in which the fraction of the NiAl/Cu co-precipitates further increases to $\sim 69\%$, which is accompanied by the fraction of the isolated NiAl particles further decreasing to $\sim 31\%$.

1-nm-thick atom maps through the centers of the two types of particle configurations are shown in Fig. 8 as a function of aging time, in which the relative positions and extents of the Al (cyan), Ni (red) and Cu (green) atoms are indicated. The first type of configuration (the left of Fig. 8a-c) is the precipitation of isolated NiAl particles, in which Ni and Al together with a considerable amount of Cu are enriched in the particles. However, the Cu atoms are near-uniformly distributed in the NiAl particles with no significant clustering. The second type of configuration (the right of Fig. 8a-c) is the precipitation of NiAl/Cu co-precipitates, in which the Cu particles are located on the outside surface of the NiAl particles. In the 0.5 h condition, the Cu particles overlaps largely with the NiAl particles and contains significant amounts of Ni and Al, indicating that the composition of the Cu particles is far from equilibrium. With the increasing aging time, the degree of overlapping between the NiAl and Cu particles becomes smaller.

The estimated compositions of the NiAl and Cu nanoparticles in different aging conditions are summarized in Fig. 9a and b, respectively. The compositions after aging for 0.5, 2 and 8 h were estimated from the central region of the particles based on information from the proximity histograms, whereas that in the 128 h condition were derived from the mass peak deconvolution method of the interior of the NiAl and Cu nanoparticles. In the 0.5 h condition, the NiAl particles contain 32.13 ± 0.57 at.% Ni, 25.38 ± 0.53 at.% Al, 9.34 ± 0.35 at.% Mn, 11.80 ± 0.39 at.% Cu and 21.34 ± 0.50 at.% Fe. The concentrations of Ni, Al and Mn increase continuously with aging time, reaching values of 49.40 ± 0.26 at.%, 31.12 ± 0.23 at.% and 11.67 ± 0.16 at.%, respectively, after aging for 128 h, whereas that of Cu and Fe decrease significantly with aging time, achieving values of 3.53 ± 0.11 at.% and 4.28 ± 0.12 at.%, respectively, after aging for 128 h. In the long-term aged condition (128 h), the ratio of Ni:(Al+Cu+Mn+Fe) is

close to ~50:50, suggesting the NiAl particles are of NiAl-type with certain amounts of Cu and Mn substitutional for partial Al. The compositions of the Cu nanoparticles are illustrated in Fig. 9b. At 0.5 h, the Cu particles are enriched in Cu (29.63 ± 2.26 at.%) but also contains significant amounts of Fe (28.79 ± 1.15 at.%), Ni (23.37 ± 1.08 at.%), Al (11.62 ± 0.81 at.%) and Mn (6.58 ± 0.53 at.%). As the aging time increases from 0.5 to 2 h, the Cu particles show only a slight change in composition. Upon further aging, the Cu concentration in the Cu particles increases to 54.67 ± 0.94 at.% at 8 h and further to 74.96 ± 0.30 at.% at 128 h. Meanwhile, the concentrations of Ni, Al and Fe decrease continuously with aging time, reaching values of 5.52 ± 0.18 at.%, 5.76 ± 0.17 at.% and 5.40 ± 0.17 at.%, respectively, after aging for 128 h. In this condition, the Cu concentration (74.96 ± 0.30 at.%) is much lower than that reported after a long-term aging (97.6 at.%) in a Fe-Cu-based steel [45], indicates that the Cu particles in the 128 h condition is still far from the equilibrium phase.

5. Discussion

The results above indicate that upon aging, the nanoscale NiAl and Cu particles undergo a rather complex evolution, involving the changes in size, number density, configuration and composition. In the following sections, the precipitation mechanism of the studied ultra-high strength steel will be discussed and also compared with previous results observed in other Cu- and NiAl-strengthened steels with relatively low Ni/Cu and Al/Cu ratios. This comparison is expected to reveal the detailed precipitation mechanism in the steels relatively high Ni/Cu and Al/Cu ratios.

We first analyze the precipitation sequence of the nanoscale NiAl and Cu particles in the steel during isothermal aging at 550 °C. At the early stage of precipitation (the 0.5 h condition),

the majority of the NiAl nanoparticles (~94% in fraction) are isolated particles with no Cu particles associated with them, and the number density of the NiAl nanoparticles ($\sim 3.9 \times 10^{24} \text{ m}^{-3}$) is more than an order of magnitude larger than that of the Cu nanoparticles ($\sim 2.5 \times 10^{23} \text{ m}^{-3}$), these indicating that the NiAl nanoparticles essentially first come out of the supersaturated solid solution. As the aging time increases, the relative number of the Cu particles located on the NiAl particle surface increases gradually from 6% at 0.5 h to 23% at 2 h and further to 69% at 8 h, suggesting that the Cu nanoparticles form after the NiAl nanoparticles in the aging sequence. In addition, the number density of the NiAl nanoparticles decreases monotonically with aging time, from $\sim 3.9 \times 10^{24} \text{ m}^{-3}$ at 0.5 h to $\sim 5.0 \times 10^{23} \text{ m}^{-3}$ at 8 h, while that of Cu nanoparticles increases from $\sim 2.5 \times 10^{23}$ to $\sim 5.2 \times 10^{23} \text{ m}^{-3}$ as the aging time increases from 0.5 to 2 h but then drops to $\sim 2.2 \times 10^{23} \text{ m}^{-3}$ upon further aging to 8 h, which further confirms that the Cu nanoparticles form at a later stage of precipitation, as compared with the NiAl nanoparticles.

It is interesting to note that although the Cu nanoparticles form after the NiAl nanoparticles in the aging sequence, a significant amount of Cu is enriched in the NiAl nanoparticles at the early stage of precipitation (see Figs. 8 and 9). Since Cu has a marginal solubility in the α -Fe matrix, it can easily be incorporated in the NiAl precipitation process. When the NiAl phase is Ni-rich, Cu has been found to be energetically favorable in occupying the Al sublattice [46]. Because the atomic radius of Cu (1.28 Å) is significantly smaller than that of Al (1.43 Å), the substitution of Cu for Al would significantly reduce the lattice misfit strain between the NiAl particles and the α -Fe (1.24 Å) matrix [47]. As a result, the critical energy for the nucleation of the NiAl particles can be reduced, thereby promoting the precipitation of Ni(Al,Cu). Therefore, the Cu solutes, enriched in the NiAl-type nanoparticles, play an important role in enhancing the precipitation of NiAl, which is similar as the role of Mn in the NiAl

precipitation [44]. Furthermore, the APT results also suggest that the majority of the Cu nanoparticles are formed by the mechanism involving the rejection of Cu solute atoms from the Ni(Al,Cu) particles. This mechanism is supported based on the facts that the Cu nanoparticles are always located on the surface of the NiAl nanoparticles, and that the degree of overlapping between the Cu and NiAl nanoparticles becomes smaller with aging time. The rejection of Cu solutes from the NiAl nanoparticles can be explained by the positive heat of mixing of the Cu-Ni pair (+4 J/m) as the driving force for the phase separation [48], accompanying the evolution of the NiAl and Cu particles towards the equilibrium state.

Based on the above discussion on the formation and evolution of the NiAl and Cu nanoparticles, the precipitation mechanism of the studied steel can be summarized as follows and schematically illustrated in Fig. 10. At the initial stage of precipitation, the NiAl nanoparticles, enriched in Ni and Al together with considerable amounts of Cu, first come out of the supersaturated solid solution; as the precipitation reaction continues, the first formation of the NiAl particles leads to the rejection of Cu solutes outwards the NiAl particles, resulting in the heterogeneous precipitation of Cu nanoparticles adjacent to the NiAl nanoparticles. Put succinctly, the precipitation sequence in the studied steel can be expressed as

which is significantly different from the one previously reported in Cu-strengthened steels, involving the process [15-26] of

In the previously reported Fe-Cu-Ni-Al-based steels with low Ni/Cu and Al/Cu ratios, the Cu particles, rather than the NiAl particles, nucleate first from the supersaturated solid solution, and both Ni and Al tend to segregate at the interface between the Cu particles and the matrix. At a

later stage of precipitation, the interfacial segregation of Ni and Al leads to the heterogeneous nucleation of NiAl at the Cu particle/matrix interface.

From the thermodynamic point of view, the precipitation sequence of different types of particles is determined by the competition of the nucleation driving force of the competing phases [36], dependent strongly upon not only the concentration of the particle forming elements but also other alloying elements that might affect the nucleation barrier. The modulating of the precipitation sequence in the steel can be explained from three aspects. First, the studied steel contains sufficiently enough Ni and Al concentrations beyond the miscibility gap for disordered bcc-ferrite and B2-ordered NiAl, which makes the independent nucleation of NiAl in the α -Fe matrix possible. Previous studies indicated that for the homogeneous precipitation of NiAl in Cu-free steels, the Ni and Al contents should be at least 2.5 and 1 wt.%, respectively [40]. In this study, the concentrations of Ni and Al in the steel (5 and 2 wt.%, respectively) far exceed the miscibility limit of the two elements, showing a high supersaturation for the precipitation of NiAl. Second, this steel has relatively high ratios of Ni/Cu and Al/Cu, as compared with the previous studied Cu-strengthened steels. As listed in Table 2, the Ni/Cu and Al/Cu ratios in previous studied alloys are usually less than 2 and 0.5, respectively, while that in the present steel are ~ 3.33 and ~ 1.33 , respectively. It is expected that the relatively high Ni/Cu and Al/Cu ratios would yield a higher chemical driving force for the precipitation of NiAl relative to that of the Cu particles. Third, APT reveals that Cu and Mn tend to partition into the NiAl nanoparticles at the early stages of precipitation by substituting for partial Al, which can significantly reduce the strain energy for the formation of NiAl nanoparticles, thereby substantially enhancing the precipitation of NiAl. In addition, as compared with other NiAl-strengthened maraging steels which usually contain high Ni and Al contents in order to form adequate NiAl particles, the

additions of Cu and Mn in the studied steel help to reduce the steel cost, because Cu and Mn are much cheaper than Ni. Therefore, the synergistic combination of Ni, Al, Cu and Mn additions play an important role in modulating the precipitation sequence from “supersaturated solid solution $\rightarrow$ Cu $\rightarrow$ Cu + NiAl” to “supersaturated solid solution $\rightarrow$ NiAl $\rightarrow$ NiAl + Cu”, leading to the formation of an extremely high number density of NiAl nanoparticles ($\sim 3.9 \times 10^{24}$ and $\sim 2.8 \times 10^{24} \text{ m}^{-3}$ at 0.5 and 2 h, respectively) as the dominant strengthening phase in the steel.

It is well known that NiAl intermetallic nanoparticles constitute one of the most effective strengthening phases (much more effective than Cu nanoparticles), because high-energy anti-phase boundaries (APB) must be created by moving single dislocations [49], thereby resulting in a high strengthening efficiency. In this study, the NiAl nanoparticles have a large number density of above $2 \times 10^{24} \text{ m}^{-3}$ and fine particle size of 1-5 nm, thereby providing a significant contribution to the ultra-high strength of the steel. In addition, the steel also contains a high number density of Cu nanoparticles ($\sim 2.5 \times 10^{23}$ and $\sim 5.2 \times 10^{23} \text{ m}^{-3}$ at 0.5 and 2 h, respectively) and a small amount of nanoscale carbides, which provide a supplement strengthening effect. The combination of the strengthening effects from the NiAl and Cu nanoparticles and nano-carbides can greatly contribute to the overall ultra-high strength of the steel. Therefore, by optimizing alloying additions of Ni, Al, Cu and Mn, controlling the precipitation mechanism, and engineering the precipitation nanostructural features, the ultra-high strength steel has been developed with a reduced Ni content, thereby being relatively cost-effective as compared with maraging steels [36]. It is anticipated that this steel with a good combination of ultra-high strength and good ductility has a great potential for structural applications. In addition, the nano-engineering approach, in principle, can be applied to explore other alloy systems for improved

performance, which provides an effective route for strengthening materials without significantly sacrificing other important properties.

6. Summary

This study presents the mechanistic understanding of the development of an ultra-high strength steel hardened by a group of nanoparticles through a computational-aided alloy design approach, and the precipitation nanostructural features and mechanical properties were carefully characterized by experimental studies mainly using APT, the state-of-the-art nanoanalytical tool. The following conclusions can be drawn from the current study:

1. The ultra-high strength steel was developed in the Fe-Ni-Al-Mn-Cu-Mo-W-Nb-C-B multi-component alloy system through a computational-aided alloy design approach. The steel exhibits a remarkable age hardening response during isothermal aging at 450-550 °C. In the peak hardening condition, the steel shows an ultimate tensile strength of ~1.9 GPa, an elongation of ~10% and a reduction in area of ~40%, indicating a good combination of ultra-high strength and good ductility.
2. APT reveals the formation of high number densities of 1-5 nm NiAl and Cu particles in the aged specimens. In the 0.5 h condition, the majority of the NiAl nanoparticles (~94%) are isolated particles with no Cu particles associated with them, and the number density of the NiAl nanoparticles is more than an order of magnitude higher than that of the Cu nanoparticles. The relative number of the Cu nanoparticles located on the NiAl particle surface increases gradually from 6% at 0.5 h to 23% at 2 h and further to 69% at 8 h. In addition, a small amount of nanoscale $\text{Fe}_3(\text{Mo,W})_3\text{C}$ - and NbC-type carbides are also detected by TEM and APT.

3. The precipitation sequence of the steel with relatively high Ni/Cu and Al/Cu ratios can be expressed as “supersaturated solid solution $\rightarrow$ NiAl $\rightarrow$ NiAl + Cu”, which is significantly different from the one previously reported in the Cu-strengthened steels with relatively low Ni/Cu and Al/Cu ratios, involving the process of “supersaturated solid solution $\rightarrow$ Cu $\rightarrow$ Cu + NiAl”. The modulation of the precipitation sequence is attributed not only to the relative high Ni/Cu and Al/Cu ratios but also the synergistic combination of Ni, Al, Cu and Mn additions, which leads to the formation of an extremely high number density of NiAl nanoparticles as the dominant strengthening phase.
4. By optimizing alloying additions of Ni, Al, Cu and Mn, controlling the precipitation mechanism, and engineering the precipitation nanostructural features, the ultra-high strength ductile steel has been developed with a reduced Ni content as compared with maraging steels, showing a great potential for structural applications.

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Figure legends

Fig. 1 Calculated phase fractions as a function of alloying addition and temperature: (a) Cu phase at 550 and 900 °C, (b) retained austenite at 550 °C, (c) δ -ferrite at 900 °C, and (d) intersections of the composition range fulfilling the design requirements.

Fig. 2 Hardness as a function of aging time at 400-550 °C for the studied steel.

Fig. 3 Room-temperature tensile stress-strain curve of the steel aged for 2 h at 550 °C and the insets showing the fracture surfaces.

Fig. 4 (a) TEM bright-field image of nanoscale $\text{Fe}_3(\text{Mo,W})_3\text{C}$ - and NbC-type carbides. The insets show a HRTEM image of a representative $\text{Fe}_3(\text{Mo,W})_3\text{C}$ -type carbide and its FFT pattern. (b) EDS spectra for the $\text{Fe}_3(\text{Mo,W})_3\text{C}$ - and NbC-type carbides.

Fig. 5 Nanostructures of the NiAl and Cu particles in the aged specimens: (a) 0.5 h, (b) 2 h, (c) 8 h, and (d) 128 h.

Fig. 6 (a) Particle radius and (b) number density of the NiAl and Cu nanoparticles as a function of aging time.

Fig. 7 Fractions of the isolated NiAl particles and NiAl/Cu co-precipitates as a function of aging time.

Fig. 8 1-nm-thick atom maps showing the Al (cyan), Ni (red) and Cu (green) atoms through the centers of isolated NiAl particles and NiAl/Cu co-precipitates in the aged specimens: (a) 0.5 h, (b) 2 h, and (c) 8 h.

Fig. 9 APT compositions of the (a) NiAl and (b) Cu nanoparticles as a function of aging time.

Fig. 10 Schematics showing the precipitation mechanism of the NiAl and Cu nanoparticles in the steel with relatively high Ni/Cu and Al/Cu ratios.

Fig. 1

Fig. 1 (cont'd)

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 5 (cont'd)

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Table 1. APT compositions of the nanoscale carbides in the 2 h condition (at.%).

carbide	C	Mo	W	Nb	Fe	Ni	Al	Mn
$\text{Fe}_3(\text{Mo,W})_3\text{C}$	16.51 ± 0.05	29.42 ± 0.08	12.68 ± 0.07	0.95 ± 0.03	37.23 ± 0.15	0.83 ± 0.02	1.16 ± 0.02	1.22 ± 0.02
NbC	41.71 ± 0.57	11.02 ± 0.37	12.56 ± 0.31	22.81 ± 0.47	9.81 ± 0.35	0.71 ± 0.15	0.62 ± 0.10	0.76 ± 0.11

Table 2. Compositions and Ni/Cu and Al/Cu ratios in Cu- and NiAl-strengthened steels (wt.%).

Cu	Ni	Al	Mn	Ni/Cu	Al/Cu	Ref.
1.37	0.82	0.03	0.49	0.60	0.02	[24]
2.00	0.75	0.30	0.75	0.38	0.15	[26]
2.09	2.83	0.68	0.50	1.35	0.33	[25]
2.50	2.50	1.00	1.50	1.00	0.40	[15]
2.50	4.00	1.00	1.50	1.60	0.40	[16]
3.00	4.00	1.50	3.00	1.33	0.50	[17]
1.50	5.00	2.00	3.00	3.33	1.33	This study