Effects of increased alloying element content on NiAl-type precipitate formation, loading rate sensitivity, and ductility of Cu- and NiAl-precipitation-strengthened ferritic steels

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Two experimental *bcc*-Cu- and B2-NiAl-precipitation-strengthened ferritic steels with 6.3 at. % and 12.4 at. % Cu+Mn+Ni+Al, 950 MPa and 1600 MPa yield strength respectively, were studied. Atom probe tomography showed that the volume fraction and number density of NiAl-type precipitates in the heavier alloyed steel (designated as *CF-9*) is ~ 60-70 times greater than those in the lighter alloyed steel (designated as *CF-2*). This is attributed to the smaller lattice misfit between these NiAl-type precipitates and the ferritic matrix in *CF-9* due to more incorporation of Mn atoms on the Al sub-lattice in the B2 NiAl unit cell. Loading rate sensitivity of hardness was measured for *CF-2*, *CF-9* and SAE-1090, which does not have *bcc*-Cu precipitates. Results show that even though *CF-2* and *CF-9* have double and triple the strength of SAE-1090 respectively, their hardness shows weaker dependence on loading rate. This is attributed to the presence of *bcc*-Cu precipitates in *CF-2* and *CF-9* providing athermal activation of nearby screw dislocation motion. Auger electron spectroscopy studies of *CF-9* samples reveal Cu segregation on grain boundaries. The observed Cu segregation is believed to be partly responsible for the lower elongation-to-failure of *CF-9* compared with *CF-2*.

1. INTRODUCTION

Some years ago, we developed a series of precipitation-strengthened steels that can be considered to be analogs of *HSLA-100* without Cr and Mo, with simplified thermal processing (hot rolling followed by air cooling). One version has 70 ksi yield strength (480 MPa) and received the ASTM A710 grade B designation and has been used recently for the construction of two bridges in Illinois [1]. The strengthening is primarily derived from the presence of semi-coherent Cu-containing precipitates. Another version, designated *NUCu-140*, has 140 ksi yield strength (965 MPa), which is achieved by addition of Ni and Al to promote the formation of NiAl precipitates [2]. Subsequently, we systematically increased the concentration of principal alloying elements (Mn, Cu, Ni and Al) with the intent to achieve higher precipitate densities and volume fractions in a series of *bcc*-Cu and B2-NiAl-type precipitation-strengthened ferritic steels, designated as *CF* steels [3]. The yield strength of *CF* steels was found to increase with the amount of principal alloying elements, reaching yield strength of 232 ksi (~1600 MPa) with 12.4 at. % alloying elements. Most of these *CF* steels have room-temperature ductility in the range of 11-30 %, higher than other commercially available steels with comparable strength [1-3].

The excellent ductility of these *CF* steels was explained by the interaction of the screw dislocations in the ferritic matrix with semi-coherent Cu-containing or -alloyed precipitates. It is hypothesized that the strain field from a semi-coherent precipitate promotes the formation of a double kink in a nearby screw dislocation [1, 4-6]. The kink segments have the characteristics of an edge dislocation, which is quite mobile in *bcc* iron, thus resulting in improved ductility and toughness. The formation of *bcc* Cu-alloyed precipitates in binary Fe-Cu is well documented and has recently been established in heavily alloyed steels [3, 7-13]. The presence of B2-NiAl-type of precipitates forming on these Cu-alloyed precipitates has also been reported in the heavily alloyed steels after aging in 500-550°C temperature range [3, 13, 14].

In this paper, we will report investigations of two outstanding issues related to these heavily Cu-alloyed *CF* steels, containing over 12 at. % of principal alloying elements (Mn, Cu, Ni and Al): strain-rate sensitivity of flow stress and copper segregation. First, our previous work demonstrated the monotonic increase of yield strength with the amount of alloying elements

due to the co-precipitation of Cu-alloyed and B2-NiAl precipitates. As indicated in the preceding paragraph, our hypothesis is that these semi-coherent precipitates provide athermal activation of screw dislocation motion, thereby slowing increase of flow stress with decreasing temperatures. Since lower temperature can be simulated at ambient temperature by testing at higher strain or loading rates, we tested this hypothesis by measuring the flow stress of lightly Cu-alloyed steels (containing ≈ 6 at. % of principal alloying elements) as a function of strain rate and comparing the data with those from *HSLA-65*, which does not contain these semi-coherent precipitates [15]. The result demonstrated that lightly Cu-alloyed steels have significantly lower strain-rate sensitivity. We would like to extend this investigation to heavily Cu-alloyed *CF* steels.

Second, while the addition of Ni and Al to form NiAl precipitates is beneficial for enhanced strength, the removal of Ni from the matrix due to precipitation may facilitate the segregation of Cu to grain boundaries – one requires a certain minimum amount of Ni in the matrix to prevent Cu segregation [16, 17]. Further, typical aging temperatures of 500-550°C used in our study fortuitously fall in the temperature range often observed to result in elemental segregation to grain boundaries [18, 19]. Experimental results and recent first-principles calculations along with computer simulations also show that Cu segregation to grain boundaries, driven by a decrease in the grain boundary energy, will have embrittling effects [18, 20-24]. Specifically, Yuasa *et al.* calculated that a Cu-segregated Fe σ_3 grain boundary will have a 27 % lower elongation-to-failure than a clean one [20]. Interestingly, their calculation also predicted that this segregation did not have any impact on flow stress. Additionally, a higher amount of Al in the matrix has been consistently shown to reduce the ductility of ferritic steels [25-27] by lowering the dislocation mobility. Therefore, we would like to investigate the effect of the addition of (Ni + Al) on the ductility of *CF* steels.

2. EXPERIMENTAL METHODS

Compositions of two alloys used in this study are presented in Table 1. *CF-2* was arc-melted and cold-swaged from a diameter of 20 mm to 8 mm. *CF-9* was produced by Sophisticated Alloys as a 22.5 kg ingot and hot-rolled. The composition was determined by spectrographic analysis. Both alloys were solution-treated at 950°C followed by water quenching and aged at

500°C and 550°C. In other experiments, *CF-9* was solution-treated at 950°C followed by aging in the temperature range of 400°C to 600°C. A Struers Duramin hardness tester was used for Vickers hardness testing, at 0.2 kgf load for 15 sec. The samples were mounted in acrylic and polished to 1 μm . Each data point is an average of 5 readings. The units of Vickers hardness number (VHN) used in this study are kgf/mm^2 .

Table 1: Composition of steels investigated in this study

		Mn	Cu	Ni	Al	C	Nb	Si	Fe	Mn + Cu + Ni + Al
CF – 2	wt. %	0.52	2.48	2.58	0.59	0.06	0.06	0.51	Balance	6.17
	at. %	0.52	2.15	2.43	1.21	0.28	0.04	1.00	Balance	6.31
CF – 9	wt. %	3.00	3.00	4.00	1.50	0.05	0.07	0.53	Balance	11.50
	at. %	2.99	2.59	3.77	3.05	0.27	0.04	1.03	Balance	12.40

3D atom probe tomography (3DAP) was used to determine the morphology, size, number density, and composition of nanoscale Cu-alloyed and NiAl-type precipitates. 3DAP studies were conducted using LEAP 4000XSi. Atom probe tomography tip blanks (0.3 mm x 0.3 mm x 12 mm) were cut using electric discharge machining and were electropolished using a standard two-step procedure: 10% perchloric acid in acetic acid at 8 to 20 Vdc at room temperature, followed by 2% perchloric acid in butoxyethanol at 8 to 15 Vdc at room temperature. Data acquisition was performed under ultrahigh vacuum ($\approx 10^{-7}$ Pa) at 65 K, with laser pulsing at 500 kHz, pulse energy being in the 40 pJ range. Data were analyzed using Image Visualization and Analysis Software. For volume fraction calculations, Cu-alloyed and NiAl-type precipitates were delineated using 10 at.% Cu and 20 at. % (Ni+Al) isoconcentration surfaces respectively. The number density of the precipitates was calculated by counting precipitates in the reconstructed volume, including fractional counts for precipitates cut by boundary surfaces of the volume.

To determine the effect of loading rate on hardness, we performed indentation on 2 mm thick polished discs of *CF-2*, *CF-9* and hot-rolled *SAE-1090* steel on an ultra-micro-indentation system. All discs were polished to one micron. The maximum load was 200 mN, and the loading rates varied from 1 to 75 mN/s.

Auger studies were performed using the PEI 660 scanning Auger microprobe on *CF-9*. The sample was prepared using the standard heat treatment – solution-treating at 950°C followed by water quench and aging at 550°C for 2 h. One sample was fractured *in situ* at a prescribed

notch at -80°C and one at room temperature. Auger analysis was performed at several selected spots of the surface, followed by argon sputter-profiling.

Compression testing was performed on MTS 810 at room temperature. Cylindrical CF-9 samples, 3 mm in diameter and 4.5 mm in height, were prepared according to ASTM E9-89a.

3. RESULTS

3.1 Aging studies and atom probe tomography

Fig. 1 shows the evolution of Vickers hardness for CF-2 as a function of time at 500°C and 550°C . The highest hardness, 380 VHN, was achieved at 500°C after aging for 2 hrs. The difference in hardness between 500°C and 550°C can be explained by the difference in precipitated volume fraction at the respective temperatures. Based on the solubilities at 500°C and 550°C , it is reasonable to assume that the precipitated volume fraction at 500°C will be higher than that at 550°C . The peak hardness condition, solution-treated at 950°C followed by water-quenching and aging at 500°C for 2 h, was selected for further atom probe tomography study.

Fig. 2 (a) is a 3D map of the distribution of Cu atoms in Cu-alloyed precipitates for CF-2 after aging at 500°C for 2h. The average volume-equivalent-radius of these precipitates is 2.0 ± 0.6 nm, the number density being $68.7 \pm 3.2 \times 10^{22}/\text{m}^3$, and the precipitated volume fraction 5.7%. Fig. 2(b) and (c) show Cu and NiAl-type precipitates delineated with 10 at. % Cu and 20 at. % (Ni+Al) isoconcentration surfaces in CF-2 and CF-9 respectively. Fig. 2 (c) [3], is shown here for comparison purposes to illustrate the differences. CF-2 and CF-9 were solution-treated at 950°C , followed by water-quenching and aging for 2 h. The aging temperature was 500°C for CF-2 and 550°C for CF-9. For CF-9, the average volume-equivalent-radius of Cu-alloyed precipitates is 3.3 ± 0.8 nm [3], about 50% greater than that in CF-2, and the precipitated volume fraction is 7.04 %. The volume fractions roughly scale with the bulk amount of Cu in the two steels, 2.59 at. % in CF-2 and 2.99 at. % in CF-9.

However, CF-2 does not show any appreciable volume fraction of B2-NiAl-type of precipitates compared to CF-9 (0.01 % compared to 7.2 %). The number density of NiAl-type precipitates (shown in green) in CF-2 is about 1/60 of that in CF-9 ($2.99 \times 10^{21}/\text{m}^3$ vs. $1.69 \times$

$10^{23}/\text{m}^3$), in spite of the lower aging temperature for *CF-2*. Apart from Fe, the major constituents of NiAl-type precipitates are Ni, Al, and Mn [3]. These three elements add up to 4.16 at. % in *CF-2*, compared with 9.82 at. % in *CF-9*. Therefore, the significantly higher number density and volume fraction of NiAl-type precipitates in *CF-9* cannot be accounted for by merely the ratio of elemental concentrations.

Our previous atom probe studies [3] suggest that Mn substitutes for Al in NiAl, consistent with the calculations by Jiao *et al.* [[13]]. Given the smaller atomic radius of Mn compared with Al, Mn substitution should result in a smaller lattice constant for Ni(Al,Mn) and hence a better lattice match with the *bcc* Fe matrix. Since *CF-9* has a higher Mn concentration than *CF-2* (2.99 vs. 0.52 at. %), Ni(Al,Mn) precipitates likely contain higher Mn concentration and therefore have smaller lattice misfit with the Fe matrix, thus a smaller nucleation barrier for the formation of NiAl-type precipitates. These observations are consistent with the study by Jiao *et al.* [13] on Fe-Ni-Al-Mn alloys.

3.2 Effect of loading rate on hardness

Generally, the flow stress of alloys increases with decreasing temperature. As discussed in the introduction section, increasing the strain or loading rate has the same effect on flow stress or hardness of steel as lowering the temperature. In this study, we compare the effect of loading rate on the hardness of *CF-2* and *CF-9*, both containing semi-coherent Cu-alloyed precipitates, and hot-rolled *SAE-1090* steel, which does not.

Fig. 3 compares the variation of hardness as a function of loading rate for these three steels, normalized by the corresponding hardness values at the lowest loading rate (1 mN/s). As the loading rate increases from 1 to 75 mN/s, the hardness of *SAE-1090* increases by a factor of 2.7, compared with 2.25 and 1.46 for *CF-9* and *CF-2* respectively. This trend has no relationship with the relative yield strength of these steels (500 MPa for *SAE-1090*, 1600 MPa for *CF-9*, and 950 MPa for *CF-2*). Along similar lines, using the Kolsky bar method, Vaynman *et al.* [15] reported the much lower strain rate sensitivity of yield strength of steels containing semi-coherent Cu-alloyed precipitates compared with *HSLA-65*. This observation is consistent with earlier hypothesis [1, 5, 6] that these precipitates facilitate the formation of double kinks in nearby

screw dislocations, thus promoting athermal activation of screw dislocation motion and slowing the increase of flow stress with decreasing temperatures or increasing strain rates.

An intriguing point is that since *CF-9* contains higher concentration of semi-coherent Cu-alloyed and NiAl-type precipitates than *CF-2*, one must wonder why *CF-9* has lower strain sensitivity as shown in Fig. 3. *CF-9* obtains its precipitation strengthening *via* various strengthening mechanisms [13, 28] including modulus mismatch, interaction with dislocation core, and order strengthening. Even though Cu-alloyed and NiAl-type precipitates help to activate double-kink formation, the motion of the resulting segments (mostly edge character) may be impeded, if the number density and size of these precipitates are large enough [29]. This is in line with our atom probe data and the observed shift in the ductile-to-brittle transition to higher temperatures in Cu-precipitate-containing reactor pressure vessel (RPV) steels due to increasing number and size of such precipitates [30].

3.3 Copper segregation

The propensity of Cu to segregate to grain boundaries and cause embrittlement in steels is well known [16, 31]. The high-temperature segregation problem, also known as hot shortness, can be mitigated by incorporating sufficient Ni so that the Ni-to-Cu ratio is greater than 0.5 [16, 32]. For both *CF-2* and *CF-9*, the Ni-to-Cu ratio is greater than one. However, our previous studies show that the elongation-to-failure for *CF-9* is significantly smaller than that for *CF-2* (4% vs. 25%) suggesting an additional mechanism at play. Embrittlement in RPV steels has been linked to the formation of Cu-rich clusters on grain boundaries and dislocations [18, 30, 33, 34]. Recent computational studies have shown that segregation of Cu to the grain boundaries is driven by a decrease in the grain boundary energy of Fe [22-24]. Specifically, molecular dynamics simulations by Gao *et. al.* suggest that it is energetically favorable to form Cu-rich clusters at a σ_3 boundary, which are subsequently absorbed by the boundary resulting in Cu segregation [23]. These segregated Cu atoms at the grain boundary weaken the Fe-Fe bond and result in grain boundary embrittlement [20]. First-principles calculations have shown that elongation-to-failure in Cu-segregated σ_3 Fe grain boundary is 27 % lower than in a clean

grain boundary [20]. This leads us to suspect that medium-temperature segregation of Cu to grain boundaries may have occurred in CF-9.

To explore this further, we conducted *in situ* fracture studies of CF-9 inside the scanning Auger microprobe. The CF-9 sample was first machined into the proper shape for *in situ* fracture. It was then solution-treated at 950°C, followed by water-quenching and aging at 550°C for 2 h. One sample was fractured at –80°C and one at room temperature. The fractured areas (marked by rectangles) from which Auger spectra were obtained are shown in Fig. 4. Both fractured surfaces show a mixture of intergranular (shown by arrows) and transgranular fracture with microvoid-coalescence-like topography [35], the former being more dominant at –80°C. Fig. 5(a) shows the Auger spectrum obtained from the surface obtained by *in situ* fracture at –80°C, averaged over two areas shown in Fig. 4(a), while Fig. 5(b) shows the corresponding spectrum by *in situ* fracture at room temperature, averaged over three areas shown in Fig. 4(b). Analysis of these spectra show the average copper surface concentration to be 3.0 ± 0.4 and 4.4 ± 0.6 at. %, respectively. Oxygen and carbon have not been included in this analysis as they are most likely due to adsorption of residual gas from the chamber. Fig. 6 shows argon sputter-profiles for two samples, one fractured at –80°C and one at room temperature. The bulk copper concentration was determined from the plateau value for both experiments to be 2.5 ± 0.3 at. %, in line with the bulk concentration of Cu in CF-9 (2.59 at. %). Significant segregation of Cu was observed in both cases.

Previous studies show that high concentrations of Al in the matrix reduce the ductility of ferritic steels by lowering the dislocation mobility [21, 25-27]. The composition of B2-NiAl-type precipitates shows an appreciable amount of Mn substituting on Al sublattice sites [3]. This will make the matrix more Al-rich than expected. Our atom probe analysis of the matrix showed that after the aging treatment, the Al content is 0.65 ± 0.03 at. % in CF-2 and 1.59 ± 0.03 at. % in CF-9. This could contribute to the lower elongation-to-failure of CF-9.

3.4 Quench tempering

According to the literature, temper embrittlement can sometimes be reversed by heating to 600°C or above, followed by quenching [19]. The reason is that the equilibrium concentration

of the segregated element on the grain boundary should approach the bulk value with increasing temperature; in this case, the higher the tempering/aging temperature, the lower the Cu concentration at grain boundaries. To explore this possibility, we prepared CF-9 samples as before (solution treatment at 950°C followed by water-quenching and aging at 550°C for 2 h), but with an additional aging/tempering step at higher temperatures. Fig. 7 shows the results of compression testing on three CF-9 samples subjected to different tempering treatments: (1) no tempering, (2) tempering at 600°C for 10 min, and (3) tempering at 625°C for 10 min. The key observation is that strain to failure increases markedly upon tempering at 600°C and 625°C.

This result could be due to the following factors - (1) Coarsening of precipitates due to heat treatment at a higher temperature. However, the small decrease in compressive yield strength after tempering for 10 mins indicates that there is very little, if any, change in the precipitation behavior. Similarly, Vickers hardness test (not shown here) performed on the alloy – with and without tempering – showed only a marginal decrease in hardness. Therefore, coarsening of precipitates cannot be a dominant factor in increasing the strain to failure. (2) The recovery of the matrix – Matrix recovery typically refers to the decrease in dislocation density, associated with a relief of internal strain energy and is manifested as a decrease in strength and increase in ductility. From Fig. 7, there is hardly any difference in the strength but a marked increase in strain to failure after tempering at 600°C and 625°C. This suggests that matrix recovery is not a controlling factor in ductility enhancement. (3) Formation of reverted austenite - The amount of reverted austenite in CF-9, predicted by thermodynamic calculations (not shown here), was found to increase by ~40% after tempering at 600°C. Therefore, the amount of reverted austenite is an important contributor to the improved strain to failure. (4) Reduced grain boundary segregation of impurities and Cu - Since Cu was the main element observed at the grain boundaries by *in situ* Auger studies, the following discussion will pertain to Cu. In general, the equilibrium segregation of a material decreases with increasing temperature, meaning at higher temperatures that composition near the grain boundary should approach the bulk composition. Hence, tempering at 600°C and 625°C should reduce the grain boundary segregation of Cu and thereby the embrittlement caused by this segregation. This experimental observation is also consistent with the calculations that show elongation-to-failure in Cu-

segregated sigma3-type Fe grain boundary is 27 % lower than in a clean grain boundary [20]. To summarize, tempering at higher temperatures increases the amount of retained austenite and reduces Cu concentration at grain boundaries, thus enhancing the elongation-to-failure of these alloys

4. CONCLUSIONS

In this study, we explored two experimental Cu- and NiAl-precipitation-strengthened ferritic steels, one being more heavily alloyed with Mn, Cu, Ni, and Al as principal alloying elements. Both the volume fraction and number density of NiAl-type precipitates are higher in the heavier alloyed steel (designated as *CF-9*) than the lighter alloyed steel (designated as *CF-2*), by a factor of 70 and 60 times respectively, much more than the ratio of the total concentration of principal alloying elements. We attribute this observation to the smaller lattice misfit between these NiAl-type precipitates and the ferritic matrix in *CF-9* due to more incorporation of Mn atoms displacing Al sites in the B2 NiAl unit cell, thereby reducing the nucleation barrier for precipitate formation.

The loading rate sensitivity of hardness of *CF-2*, *CF-9*, and plain carbon steel SAE-1090 was measured. *CF-2*, the lighter alloyed steel, shows the least sensitivity towards loading rate, consistent with earlier hypothesis that semi-coherent Cu precipitates provide athermal activation of screw dislocations. *CF-9*, though three times the strength of SAE-1090, shows loading rate sensitivity intermediate between *CF-2* and SAE-1090. We believe that its higher loading rate sensitivity than *CF-2* is due to the significantly higher number density of Cu- and NiAl-type precipitates in *CF-9* as noted above.

Auger electron spectroscopy studies of *CF-9* samples fractured *in situ* reveal the Cu segregation on grain boundaries. This segregation, driven by a reduction in the grain boundary energy, can be a result of aging in the temperature range of 500°C-550°C. This could provide a partial explanation of the lower elongation-to-failure of *CF-9* compared with *CF-2*.

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Fig. 1: Evolution of Vickers hardness as a function of time for *CF-2* after solution treatment at 950°C, followed by water-quenching and aging at 500°C and 550°C.

Fig. 2: (a) 3D atom map of *CF-2* showing Cu-alloyed precipitates. The sample was solution-treated at 950°C, followed by water-quenching and aging at 500°C for 2 hrs. Only Cu atoms are shown for clarity. (b) Cu and NiAl-type precipitates delineated with 10 at. % Cu and 20 at. % (Ni+Al) isoconcentration surfaces derived from *CF-2*. (c) Cu and NiAl-type precipitates delineated with 10 at. % Cu and 20 at. % (Ni+Al) isoconcentration surfaces derived from *CF-9* [3] shown for comparison. *CF-9* was solution-treated at 950°C, followed by water-quenching and aging at 550°C for 2h.

(a)

(b)

Fig. 3: Relative hardness of (a) CF-2 and SAE-1090 and (a) CF-9 and SAE-1090 as a function of loading rate. Relative hardness is defined as the ratio of hardness at each loading rate to that at a loading rate of 1 mN/s.

(a)

(b)

Fig. 4: Secondary electron images obtained from *CF-9* after *in situ* fracture at (a) -80°C and (b) room temperature in vacuum. The arrows in (a) point to regions showing intergranular fracture. Areas used for analysis are marked with rectangles. *CF-9* was solution-treated at 950°C followed by water-quenching and aging at 550°C for 2 h.

(a)

(b)

Fig. 5: Auger spectra obtained from CF-9 after *in situ* fracture under vacuum at (a) -80°C , averaged over two rectangular areas shown in Fig. 4(a); (b) room temperature, averaged over three rectangular areas shown in Fig. 4(b).

Fig. 6: Argon sputter-profile of copper concentration as a function of distance below the surface obtained by *in situ* fracture of CF-9 under vacuum at -80°C and room temperature. CF-9 was aged at 550°C for 2 h.

Fig. 7: Compressive stress vs. strain curve obtained from *CF-9* that has been solution-treated at 950°C, followed by water-quenching and aging at 550°C for 2 hours, followed by no further tempering, tempering at 600°C for 10 min, and tempering at 625°C for 10 min.

Graphical Abstract

CF-9 has a higher amount of alloying elements (Cu, Mn, Ni, and Al) than CF-2. More Mn is incorporated into NiAl, displacing Al. This substitution reduces the lattice misfit with the Fe matrix and hence nucleation barrier, resulting in more NiAl-type precipitates in CF-9. This increases the loading rate sensitivity in CF-9 because the precipitates impede the motion of edge dislocations. Additionally, Cu segregation is observed by *in situ* Auger studies which partially explains the lower ductility of CF-9.