Interstitial Strengthening of a f.c.c. FeNiMnAlCr High Entropy Alloy

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ABSTRACT

The effects of adding boron or carbon on the microstructure and room-temperature mechanical properties of a new single-phase f.c.c. high entropy alloy $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ are presented. Remarkably, 1.1 at. % carbon in solution not only increases the yield strength (by a factor of 2), but also increases the elongation to failure (from ~41% to 50%) and the work-hardening rate. Surprisingly, the latter increases with increasing strain up to a strain of 35%. When fine-grained (4.7 μm), the C-doped HEA exhibits a yield strength of 557 MPa.

Keywords: High-entropy alloys; interstitial effects; mechanical properties.

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INTRODUCTION

High-entropy alloys (HEAs), which have been defined as multicomponent alloys containing a minimum of five metallic elements with amounts in the range 5-35 at. % [1], have elicited growing interest since some can show high strength [2], high ductility [3] and very high fracture toughness values, particularly at low temperatures [4]. Another interesting feature of HEAs is their sluggish diffusion, which means that, following cold work, recrystallization requires high annealing temperatures and can result in small grain sizes [3,5,6].

In contrast to substitutional strengthening, little attention has been paid to interstitial strengthening in HEAs except for a study by Wu et al. [7] of a single addition of 0.5 at. % carbon to the most studied HEA FeNiCoCrMn [2,3,6], although in that case it is unclear whether all the carbon was in solution. In this note, we present the effects of the interstitial elements carbon and boron on the novel f.c.c. HEA $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$. In particular, we show that carbon not only substantially increases the yield strength, but also increases both the work-hardening rate and the ductility.

EXPERIMENTAL

~65g ingots of nominal atomic composition $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ undoped, or doped with carbon or boron were produced from 99.8% Fe, 99.95% Ni, 99.8% Mn, 99.8% Al and 99.8% Cr via arc-melting. Alloys containing ~1 at. % C, and 0.5 or 1 at. % B were produced by adding FeC or FeB, respectively. The composition of the carbon-containing ingot was determined by Chicago Spectro Service Laboratory, Inc, Chicago, IL.

Specimens for examination by scanning electron microscopy and transmission electron microscopy were prepared using previously established techniques [8].

Dog-bone-shaped tensile test specimens (gauge length -10 mm; width -2.54 mm; and thickness ~1.27 mm) were machined from the ingots. Three tensile tests were performed for each alloy at a constant displacement rate of 0.005 mm s^{-1} , corresponding to an initial strain rate of $5 \times$

10^{-4} s^{-1} . The strain determined during loading from the crosshead displacement, was corrected by the strain measured directly from the specimen after fracture. The resulting engineering stress-engineering strain curves were then converted into true stress-true strain curves.

RESULTS AND DISCUSSION

Figure 1(a, c and d) shows backscattered electron (BSE) images of the as-cast alloys. The undoped alloy and the C-doped alloy are single phase with grain sizes, measured using the linear intercept method, of $\sim 120 \text{ }\mu\text{m}$. In contrast, both the nominally 0.5 and 1 at. % B containing alloys, which also had grain sizes of $\sim 120\text{-}150 \text{ }\mu\text{m}$, contained large long precipitates some greater than $10 \text{ }\mu\text{m}$ in length. Bright field TEM imaging confirmed that the undoped and carbon-doped alloys were single phase and selected area diffraction showed that the HEA was f.c.c., see **Figure 1(b)**. Chemical analysis of the carbon-containing HEA by Chicago Spectro Service Laboratory, Inc. showed that it contained 1.1at. % C.

Figure 2(a) shows engineering stress-true strain for each of the HEAs strained to failure under tension. The undoped alloy showed a yield stress, σ_y , of $159 \pm 11 \text{ MPa}$ and an elongation to failure, ϵ_f , of $40.8 \pm 2.5\%$. The boron additions produced very little strengthening: σ_y increased to $174 \pm 10 \text{ MPa}$ and $186 \pm 6 \text{ MPa}$ for 0.5 at. % B and 1 at. % B, respectively. Given that the boron appears to be present as large precipitates the small strengthening effect is not surprising. However, these large precipitates produce a reduction in ϵ_f to $37.0 \pm 1.7 \%$ and $31.1 \pm 1.4\%$ for 0.5 at. % B and 1 at. % B, respectively. In sharp contrast, the 1.1 at. % carbon addition more than doubles σ_y to $355 \pm 7 \text{ MPa}$. This represents an increase in σ_y per at. % carbon, $\Delta\sigma_y/\Delta c$, of $178 \text{ MPa/at. \% C}$, which is significantly greater than that found for carbon strengthening of $120 \text{ MPa/at. \% C}$ in the much-studied HEA FeNiCoCrMn [7] and of $26\text{-}42 \text{ MPa/at. \% C}$ determined for TWIP steels [9,10]. Surprisingly, this large strength increase is accompanied by an increase in ϵ_f to $49.5 \pm 0.6\%$, and the fracture strength increased from $381 \pm 9 \text{ MPa}$ to $754 \pm 14 \text{ MPa}$. Table 1 summarizes the room temperature mechanical properties for each HEA.

Figure 2(b) shows the true stress and work hardening rate, WHR, as a function of true strain for the undoped and 1.1 at. % carbon-doped alloys. For the undoped alloy the WHR is almost constant up to a strain of 20%, after which it decreases with further increases in strain. The behavior of the HEA containing 1.1 at. % C is quite different. The WHR increased with increasing strain up to a strain of ~ 35 at. %. At a strain of 20% the WHR in the undoped alloy is 1179 MPa , whereas that for the alloy containing 1.1 at. % C is 1880 MPa . The WHR in the latter alloy increases to a maximum of 2236 MPa (almost twice that of the undoped alloy), which is about $G/40$ (assuming a value of G of 80 GPa). A value of $G/40$ for the WHR is typical of many f.c.c. metals [11] or f.c.c. HEAs [3,12]. We note that in TWIP steels, steels with low carbon contents show a declining WHR with increasing strain, whereas steels with high carbon contents show a WHR that is largely independent of strain or, possibly increases slightly with increasing strain [10]. In TWIP steels this change in behavior is related to the occurrence of mechanical twinning in alloys with higher carbon contents.

Apart from increases in strength due to a reduction in grain size, most methods that increase σ_y of metals decrease ϵ_f . Surprisingly, in the carbon-doped HEA studied here the addition of carbon not only increases σ_y but also leads to an $\sim 25\%$ increase in ϵ_f . **The increase of yield strength can be ascribed to the interstitial strengthening effect from the dissolved carbon atoms. The carbon atoms have a substantially smaller size than any of the metal atoms in the HEA and will thus produce a substantial strain field, with which gliding dislocations will**

interact, that arises from the size difference of the atoms [13]. Phenomenologically, the observed increase in ductility can be related to the work-hardening rate $d\sigma/d\varepsilon$. The onset of necking occurs when $d\sigma/d\varepsilon = \sigma$. The increase in $d\sigma/d\varepsilon$ due to carbon addition thus increases the stress at which necking instability will occur, which leads to the increase of ductility. This again is somewhat similar to behavior in TWIP steels [10,14] where increasing carbon and manganese increase the extent of deformation twinning, which increases ε_f , but it is in sharp contrast to the behavior of the HEA FeNiCoCrMn where the addition of 0.5 at. % carbon, while producing a large increase in σ_y , produces a substantial decrease in ε_f from ~75% to 40% [7]. This difference in behavior may be because both the carbon-free [4,15] and carbon-doped [7] FeNiCoCrMn exhibit deformation twinning, and, thus, the decrease in ε_f in the carbon-doped HEA is simply related to the substantially greater fracture strength.

Figure 3 shows secondary electron (SE) images of the fracture surfaces of the alloys strained to failure. The undoped alloy shows dimple-type ductile rupture typical of a f.c.c. alloy that shows substantial tensile ductility. The fracture surfaces of the boron-doped alloys are similar but on a finer scale. Surprisingly, the carbon-doped HEA, even though it shows higher ductility than the undoped alloy, shows a smoother fracture surface than the undoped alloy, but with clear evidence of local plasticity on the fracture surface.

Because the HEAs had large grain sizes, there was likely very little grain size strengthening. Since the HEAs show substantial ductility, we examined whether thermo-mechanical processing could be used to reduce the grain size of the promising C-doped HEA and, hence, increase the strength. Thus, this C-doped HEA was cold rolled to a 70% reduction thickness and annealed at 1000°C for 1 h. This heat treatment recrystallized the HEA and produced a grain size of 4.7 μm . Tensile testing of this alloy showed a substantial increase in σ_y to 557 ± 15 MPa compared to the as-cast alloy of 355 ± 7 MPa. Usually reducing the grain size is the one way to both increase σ_y and improve the ductility. However, for this C-doped HEA the reduction in grain size decreased ε_f from 49.5 ± 0.6 % from the as-cast value to 26.7 ± 2.0 %.

Figure 4 is a plot of room temperature ε_f versus ultimate tensile strength for a variety of steels. Also shown on the plot are the room temperature ε_f and ultimate tensile strength of fine-grained CoCrFeMnNi [14], which has been the most studied HEA thus far [2,3]. The values for both the as-cast and the recrystallized C-doped alloy are shown on the plot. Interestingly, this alloy occupies an interesting space better than most advanced steels, with the added feature that it contains several at. % of both aluminum and chromium, thus likely providing it with the character of a f.c.c. stainless steel.

CONCLUSIONS

We have shown that the addition of 1.1 at. % carbon to the novel f.c.c. HEA $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ produces not only a substantial increase in strength, but also an increase in ductility and work-hardening rate. The mechanical properties of the 1.1 at. % carbon doped alloy outperforms TRIP steels, but with the likely oxidation and corrosion resistance imparted by the presence of both aluminum and chromium.

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Table

Table 1 Mechanical properties (yield stress, ultimate tensile strength and elongation) for boron and carbon doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs at room temperature. The error bars were calculated from three tests on each alloy.

Alloy	Yield stress (MPa)	Ultimate tensile strength (MPa)	Elongation (%)
Fe _{40.4} Ni _{11.3} Mn _{34.8} Al _{7.5} Cr ₆	159 ± 11	381 ± 9	40.8 ± 2.5
Fe _{40.4} Ni _{11.3} Mn _{34.8} Al _{7.5} Cr ₆ + 0.5 at% B	174 ± 10	455 ± 10	37.0 ± 1.7
Fe _{40.4} Ni _{11.3} Mn _{34.8} Al _{7.5} Cr ₆ + 1 at% B	186 ± 6	519 ± 16	31.4 ± 1.4
Fe _{40.4} Ni _{11.3} Mn _{34.8} Al _{7.5} Cr ₆ + 1.1 at% C 120 µm	355 ± 7	754 ± 14	49.5 ± 0.6
Fe _{40.4} Ni _{11.3} Mn _{34.8} Al _{7.5} Cr ₆ + 1.1 at% C 4.7 µm	557 ± 15	1041 ± 13	26.7 ± 2.0

Figures

Figure 1. BSE images of (a) ~1.1 at. % carbon-doped, (c) 0.5 at. % boron-doped, and (d) 1 at. % boron-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$. (b) is a TEM image of the 1.1 at. % carbon-doped HEA with an inserted selected area diffraction pattern showing that the alloy is f.c.c.

Figure 2. (a) Engineering strain-stress curves for the undoped, ~1.1 at. % carbon-doped, 0.5 at. % boron-doped, and 1 at. % boron-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$; (b) true stress and work-hardening rate as a function of true strain for the undoped and ~1.1 at. % carbon-doped HEA.

Figure 3. SE images of the fracture surfaces of (a) undoped, (b) ~1.1 at. % carbon-doped, (c) 0.5 at. % boron-doped, and (d) 1 at. % boron-doped $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$.

Figure 4. Room temperature elongation versus ultimate tensile strength for a variety of steels and for the HEA CoCrFeMnNi. The values for $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ containing 1.1 at. % C with two different grain sizes are indicated. The data for the steels are from [16] and for the CoCrFeMnNi HEA is from [14].