Microstructure and properties of CoCrFeNi-based multi-principal element alloys containing C and Sc

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ABSTRACT

A series of novel CoCrFeNi-based high-entropy alloys containing Sc and C were designed. These HEAs exhibited hardness, fracture toughness and wear resistance comparable or better than a range of selected benchmark systems. Microstructurally, we observed composite microstructures comprising variously a Sc-rich intermetallic phase, a sigma phase and an FCC solid solution phase within which precipitated M23C6 carbides. The Sc-rich intermetallic phase possessed a stoichiometry close to (Co, M)2(Sc, M), where M = Ni and Fe. As the carbon content increased, the hardness levels ‘softened’ from 799 VHN (C-free) to 674 VHN (C = 4 at.%), though the fracture toughness was increased ~ 112%. At the same time, the specific wear rate was enhanced from 0.33 × 10⁻³ to 0.14 × 10⁻³ mm³/(N m)⁻¹. The effectiveness of these microstructures in balancing high hardness, crack deflection and a relatively low wear rate was attributed to the enhanced stability of the FCC solid phase as the C content was increased.

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Introduction

High-entropy alloys (HEAs), also known as multi-principal element alloys (MPEA), have emerged as an exciting new class of materials [1, 2]. HEAs, especially CoCrFeNi-based HEAs, exhibit remarkable mechanical properties at room temperature and even better properties in the cryogenic regimes, as well as good wear resistance and other properties [3–8]. The majority of the research on HEAs has been focused on CoCrFeNi-based alloys and the addition of various fifth elements to investigate the potential for improved mechanical properties [3, 9]. For example, adding Mn, which has a small atomic mismatch, results in an equiatomic quinary CoCrFeNiMn alloy that preserves a single-phase face-centred cubic (FCC) structure with lattice parameter $a = 0.359$ nm [10] that exhibits remarkable fracture toughness, especially at cryogenic temperatures [4, 11, 12]. On the other hand, the addition of Nb, which has a large atomic misfit, leads to the formation of a ductile FCC phase with lattice parameter $a = 0.3606$ nm (compared with $a = 0.3581$ nm in Nb free sample), and a second Nb-rich Laves intermetallic phase embedded in the FCC matrix [13]. These multi-phase HEAs have exceptional hardness and wear properties [14–16]. Jiang et al. [17] measured hardness and yield strength values of 515 VHN and 1745 MPa, respectively, in a CoCrFeNiNb HEA. However, as the hardness increases, the ductility and fracture toughness of the multi-phase HEAs decrease more rapidly than the diminishment observed in the single phase FCC CoCrFeNiMn alloys. Furthermore, both Mn and Nb are relatively heavy transition elements, which can be undesirable in structural materials.

The introduction of interstitial elements such as oxygen (O) [18], nitrogen (N) [19] and carbon (C) [20] has also been widely investigated. Of these, C is the most studied interstitial elemental addition to HEAs [21]. For example, Stepanov et al. [22] investigated the effects of the C content on the CoCrFeNiMn HEAs and revealed a 25% increase of the ultimate tensile strength
compared with similarly processed C-free HEAs. Wang et al. [23] demonstrated an increase in tensile elongation in a Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_{6} HEA containing 1.1 at.% C compared to the C-free alloy. The addition of C has been shown to alter the phase stability and stacking fault energy of HEAs and has consistently demonstrated excellent potential to expand their structural properties [24, 25].

In this contribution, we have investigated the novel combination of scandium (Sc) as a substitutional element, in combination with C as an interstitial elemental addition to the familiar CoCrFeNi-based alloy. Sc was of particular interest as it has a large atomic radius but is one of the lighter transition metal elements and is widely associated with a strong interaction with vacancies as utilised in Sc-bearing Al-alloys gaining acceptance in the automobile and aerospace industries [26, 27].

Materials and methods

Materials processing and sample preparation

Three alloys of composition (CoCrFeNiSc)_{100-x}C_x with C contents of x = 0, 2 and 4 at.% designated as alloys C0, C2 and C4, respectively, were prepared separately by arc melting. The raw materials were 99.99% purity cobalt (Co), iron (Fe), nickel (Ni), scandium (Sc), 99.5% purity chromium (Cr) and graphite (C) melted in an argon (Ar) atmosphere. Each alloy was remelted five times to improve homogeneity before being sectioned into smaller pieces using a diamond cutting wheel. Offcuts from each alloy were mechanically ground to 4000-grit sandpaper and polished to a mirror-like surface using successively finer diamond and silica suspensions, gradually down to a 0.25-μm silica suspension solution. Finally, the specimens were ion-milled using a Gatan PECS II system under 2 kV Ar ions.

Materials characterisation methods

X-ray diffraction (XRD) was performed using a PANalytical X’Pert Powder Cu source X-ray diffractometer between 30° and 90°. A Zeiss Ultra scanning electron microscope (SEM) with ancillary energy-dispersive X-ray spectroscopy (EDXS) and electron backscatter diffraction (EBSD) detectors was used to investigate the microstructures. Hardness measurements were taken using a LECO Vickers Hardness Tester (LV700 AT) with a load of 3 kg and a dwell time of 15 s. The mean value of five indentations was used to report hardness values and associated errors [28]. The Vickers hardness indentations were also assessed using SEM to evaluate the indentation shapes and crack lengths. Values for the fracture toughness (K_{IC}) of these samples were then estimated based on the Palmqvist method for the estimation of toughness using the length of the cracks formed by the hardness indenter by applying the following formulae [29–31]:

\[ K_{IC} = 0.0028 \times \sqrt{\frac{1000 \times H \times g^2 \times M}{L_{Tol}}} \]  
\[ L_{Tol} = L_1 + L_2 + L_3 + L_4 \]

where H is the hardness (VHN), L_{Tol} is the sum of crack lengths from the corner of indentation expressed as mm, M is the applied load (kg), and g is the acceleration due to gravity (9.81 m s^{-2}).

A ball-on-disc sliding method was used on a commercial tribometer (NANOVEA-MT/60/NI) to assess the wear resistance of these alloys. Tungsten carbide balls with a radius of 2.38 mm were used, and each test was carried out under 20 N for 30 min with a sliding speed of 0.05 m s^{-1} in air at room temperature. The specific wear rate was calculated according to Eq. (3):

\[ W_s = \frac{\Delta m}{\rho \times F_N \times L} \]  

where W_s corresponds to the specific wear rate (mm³/N m), Δm is the weight loss after the test (g), ρ is the density of the material (g mm⁻³), F_N is the force applied on the sample (N), and L is the sliding length (m). Transmission electron microscopy was conducted using a JEOL 2200 TEM, operating at an accelerating voltage of 200 kV. Atom probe tomography (APT) was conducted using CAMECA LEAP3000Si operating in voltage mode at 50 K, 20% pulse fraction, 200 KHz pulse rate and evaporation rate of 0.2 [32]. Specimens for TEM and APT were prepared using standard techniques.

Results and discussion

Mechanical properties

Figure 1a charts values for the specific hardness (hardness/VHN) of the C0, C2 and C4 alloys and provides
a comparison to values for the relevant individual elements, binary alloys, the CoCrNi-based ternary and Fe-bearing quaternary HEAs, and certain refractory HEAs taken from the literature [33–42]. The specific hardness of all three alloys C0, C2 and C4 was higher than the binary alloys and the other HEAs possessing similar densities. The specific hardness values were almost 1.5 times larger than Ti–6Al–4V (75 VHN cm$^3$ g$^{-1}$), ~ 5 times greater than the single phase FCC CoCrFeNiMn (22 VNH cm$^3$ g$^{-1}$) and ~ 6 times greater than the CoCrFeNi base alloy (18 VNH cm$^3$ g$^{-1}$). Figure 1b summarises the estimates of the fracture toughness of these alloys in comparison to values from the literature of other major HEAs and relevant alloys [43–51] using different methods. The C0 alloy exhibits a hardness of 799 VHN and a fracture toughness of 27.6 MPa m$^{1/2}$. The C-bearing alloys exhibit lower hardness but higher apparent fracture toughness. Alloy C2 possessed a hardness of 705 VHN, and our estimate of the fracture toughness was almost twice that of the alloy C0, reaching 54.0 MPa m$^{1/2}$. At 4 at.% C, the hardness decreased by 4% compared to C2, while the fracture toughness increased a further 8%. The hardness of alloy C4 was ~ 15% lower than alloy C0, and the fracture toughness was ~ 112% higher. Figure 1c presents the specific wear rates of the HEAs introduced here compared to other relevant alloys [52–55]. The specific wear rates of the alloys C0, C2 and C4 were $0.33 \times 10^{-3}$, $0.32 \times 10^{-3}$ and $0.14 \times 10^{-3}$ mm$^3$ (N-m)$^{-1}$, respectively. This is better than the specific wear rate of the CoCrFeNi alloy ($0.4 \times 10^{-3}$ mm$^3$ (N-m)$^{-1}$). The average friction coefficient of these alloys ranged between 0.65 and 0.74. The wear resistance trended in direct proportionality with the apparent fracture toughness such
that alloy C4 exhibited the highest fracture toughness and outstanding wear resistance. Here, we point out that the literature cited in our compilations in Fig. 1 contains the details of the measurement techniques variously used to assess the wear resistance, hardness and fracture toughness. The techniques were not identical, and we acknowledge that there is some potential for technique-dependent variations between the studies compiled. In the absence of unitary standard measurements for these values, we have carefully selected the studies for these compilations both to summarise the state of the art and to provide guidance in terms of how our measurements benchmark to similar systems.

The relationship between microstructure and mechanical properties

The XRD spectrum (supplementary) identified the presence of the FCC matrix phase commonly reported in CoCrFeNi HEAs (Fd\textit{3}m, \(a = 0.358\) nm) [13], an intermetallic (IM) phase with a Co\textit{3}Sc type cubic structure (Fd\textit{3}m, \(a = 0.690\) nm) and a tetragonal Fe\textit{1.01}Cr\textit{0.99} type sigma phase (P\textit{4}/\textit{2}Imn, \(a = 0.878, c = 0.456\) nm) in the C0 alloy [56]. Additional peaks for the FCC M\textit{23}C\textit{6} carbide phase (Fm\textit{3}m, \(a = 1.059\) nm) [57] were detected in both the C2 and C4 alloys. With increasing C content, the lattice parameter of the FCC solid solution phase increased \(\sim 0.5\%\) from 0.357 to 0.359 nm, and the peaks from the sigma phase diminished in height indicating a reduction of its phase fraction.

Figure 2 provides the EBSD and EDXS of the three HEAs. The data in Fig. 2a–c confirm that C effectively reduced the phase fraction of the sigma phase in this system from 35.4\% in alloy C0 to 6.3\% in alloy C2 and \(\sim 0.1\%\). Figure 2 further reveals that the IM phase fraction was increased from 41.2\% (C0) to 54.0\% (C2) and then unchanged from C2 to C4. In terms of the FCC phase, Fig. 2 reveals that, from C0 to C2, the phase fraction of the FCC phase increased from 18.9 to 26.8\%.

The hardness trends observed in these experimental alloys, where we report an 11\% softening from alloy C0 (799 VHN) to C2 (705 VHN) and a further 4\% softening from alloy C2 to C4 (674 VHN), are attributed mainly to the increased stability of the relatively soft FCC phase, which replaced the significantly harder sigma phase. Based on other reports [58], the hardness of the sigma phase is \(\sim 957\) VHN and the M\textit{23}C\textit{6} carbide phase is \(\sim 1250\) VHN. On the other hand, the hardness of the FCC phase has been reported as \(\sim 120\) VHN [59] and it can also be expected to be relatively ductile. The compositing of the hardness is overall significant, and we note that the occurrence of the very hard M\textit{23}C\textit{6} carbide phases within the softer FCC matrix. This results in a situation whereby, notwithstanding the significant increase in the phase fraction of the softer FCC phase, the overall hardness changes by only \(\sim 16\%\) overall between the three alloys.

Although the addition of the C led to microstructural changes that affected only a minor softening of the alloys, these changes brought about a significant increase the fracture toughness (Fig. 2a–c.) In the C0 sample, as shown in Fig. 2a, we observed a coarse lamellar microstructure comprised of the IM phase and the sigma phase with residual FCC phase occurring at the sigma-IM phase interfaces. The introduction of C to the level of 2 at.\%, as shown in Fig. 2b, brings about a blocky-type microstructure and the IM phase is now enveloped by the FCC phase which also contains M\textit{23}C\textit{6} carbide precipitation. Figure 2c provides the EBSD map for the alloy containing 4 at.\% C, and it is dominated by coarse lamella of the IM phase in the FCC phase, with M\textit{23}C\textit{6} carbide precipitation evident in the FCC solid solution phase.

Figure 2d provides an SEM image of a crack emanating from the corner of a hardness indent in the sample C4 and reveals that the crack prefers to propagate through the IM phase. The length of these cracks was used to estimate of the fracture toughness as described above. We found that the mean crack length in the C0 samples was 59.31 \(\mu\)m and this value decreased sharply by 77\% to 13.67 \(\mu\)m after the introduction of 2 at.\% C. We suggest that the microstructure is a key factor in the improvement of the fracture toughness here, as has also been reported in other systems [60]. In alloy C0 (Fig. 2a), the IM phase occurs as coarse globules and is in direct contact with the sigma phase throughout. The occurrence of these two intermetallic phases in direct contact appears to offer an easy crack pathway and consequently, lower fracture toughness. The addition of 2 at.\% C (Fig. 2b) and the associated replacement of the brittle sigma phase by the more ductile FCC solid solution phase that contains a dispersion of M\textit{23}C\textit{6} carbides results in an inhibition of the crack.
propagation. This was also the case in alloy C4 (Fig. 2c–d), and it is apparent that the FCC phase changes the direction of crack propagation, especially where exists precipitation of M23C6 carbide. The result is a further reduction of the extension of the crack (Fig. 2d). As indicated from the XRD data, the addition of C slightly distorted the FCC crystal lattice, which appears to have increased the amount of plastic deformation required to propagate the crack [61]. Correlative EDXS maps were also recorded from the alloy C4 (Fig. 2f–i). The FCC solid solution was observed to be enriched in Cr and Fe, the M23C6 carbides were enriched in Cr, while the Sc rich IM phase was enriched with significant Co and

Figure 2 SEM-based imaging from the alloys investigated. a–d are EBSD maps, as follows: a CrNiFeCoSc-based alloy (C0), b CrNiFeCoSc-2 at.%C alloy (C2), c CrNiFeCoSc-4 at.%C alloy (C4), d crack propagation in alloy C4. e–i are EDXS maps from sample C4 as follows: e Cr, f Fe, g Co, h Sc and i Ni.
Ni. Thermodynamic calculations of the effect of C-additions to CoCrFeNi-based [62] HEAs indicate that both FCC and M\textsubscript{23}C\textsubscript{6} carbide can form at temperatures \( \sim 1000 \, ^\circ\text{C} \), whereas the sigma phase is formed between \( \sim 500 \) and \( \sim 800 \, ^\circ\text{C} \) [63]. In our current study, 2 at.% carbon enabled equilibrium between both the FCC phase and the M\textsubscript{23}C\textsubscript{6} phase and we suggest that the sigma phase precipitated during the cooling process. Interestingly, the co-existence of these phases has also been studied in Cr-bearing steels [64]. From our EDXS results, both the carbide and sigma phases were Cr rich. The thermodynamic and kinetic pre-requisites for the formation of M\textsubscript{23}C\textsubscript{6} carbide and sigma phase are such that the volume fraction of both of these phases was reduced, which resulted in enhanced FCC stability.

**Figure 3** TEM and APT analysis of alloy C4. **a** and **b** TEM bright-field images with inset SAED patterns of the Sc-rich IM, the Fe-rich FCC solid solution phase and the M\textsubscript{23}C\textsubscript{6} carbide phases. Some dislocation debris remains in the FCC phase. **c** APT atom map of an interface between the Sc-rich IM phase and the M\textsubscript{23}C\textsubscript{6} phase. An SEM image of the corresponding APT tip is inset. **d** Atom map and the element concentration profile across the phase boundary in (**c**). The concentration profiles for each element are plotted as the trace of the mean with the standard error shaded.
TEM and APT analyses were conducted on alloy C4 to better understand this microstructure. As is evident in the TEM images provided in Fig. 3a–b, the Cr-rich M23C6 precipitation that occurred in the FCC solid solution phase possessed an ellipsoidal morphology. The TEM images indicate that these carbides were between 100 and 300 nm in their longest dimension. The SAED pattern inset in Fig. 3b indicates that the FCC phase and M23C6 carbide exhibit orientation relationships such that \( \{111\}_{\text{FCC}}// \{111\}_{\text{M23C6}} \) and \( <01\overline{1}>_{\text{FCC}}//<01\overline{1}>_{\text{M23C6}} \). An APT analysis at the interface between the Sc-rich IM phase and an M23C6 carbide is provided in Fig. 3c–d. The carbide appears enriched in both Cr and Fe, and there is some evidence of a C-rich region at the phase boundary. We have used this analysis to estimate the Sc-rich IM phase as comprising 28.7 at.% Sc, 35.3 at.% Ni, 20.2 at.% Co, and 12.7 at.% Fe suggestive of a \((\text{Co, M})_2(\text{Sc, M})\) stoichiometry, where \( \text{M} = \text{Ni} \) and Fe. Strengthening/hardening from carbide precipitation as well as changes to the phase fractions are put forward as the critical factors that explain the simultaneous reduction in hardness and increase fracture toughness with increasing C content. The fact that M23C6 carbide formed instead of the sigma phase is demonstrated in Fig. 2a, b. Both phases are hard but brittle. The overall fraction of these phases reduced with increasing FCC phase fraction. For example, the more local observations in Fig. 2d, Fig. 3b, d, the embedded hard M23C6 carbides were dispersed in the relative soft FCC phase. This seems to achieve a desirable balance in hardness and fracture toughness.

The changes in the type and distribution of the microstructural phases also contributed to changes in the measured wear resistance. Compared to the CoCrFeNi-based alloy, where the microstructure was dominated by the sigma phase, the specific wear rate of the C4 alloy decreased \( \sim 65\% \). From the Sc-bearing alloy C0 to the Sc + C-bearing alloy C4, the specific wear rate decreased more than 50%. The replacement of the sigma phase by the carbides within the FCC phases played a key role as does the toughness of the Sc-bearing IM phase.

Conclusions

In summary, we have measured the hardness, fracture toughness and the specific wear rate of a novel series of CoCrFeNi HEAs to which Sc and C were added. The new Sc- and C-bearing HEAs not only maintained high hardness, but also exhibited higher fracture toughness and improved wear resistance than many comparable systems.

Microstructurally, we observed a Sc-rich intermetallic phase of approximate composition 28.7 at.% Sc, 35.3 at.% Ni, 20.2 at.% Co, and 12.7 at.% Fe, and a FCC solid solution phase within which occurred M23C6 carbides, which was effective at supporting high hardness, deflecting cracks and a low wear rate.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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