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A comparison of the dry sliding wear of single-phase f.c.c. carbon-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ and CoCrFeMnNi high entropy alloys with 316 stainless steel



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ARTICLE INFO	A B S T R A C T
Keywords: High entropy alloys Wear Oxidation X-ray photoelectron spectroscopy Atom probe tomography	The dry sliding wear behaviors of the face-centred cubic (f.c.c.) high entropy alloys carbon-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ and equiatomic CoCrFeMnNi were determined under ambient conditions and compared with that of 316 stainless steel at two sliding velocities and in argon at a slow sliding velocity. Scanning electron microscopy, energy dispersive X-ray spectrometry, electron backscattered diffraction, X-ray photoelectron spectroscopy, and atom probe tomography analyses were employed to characterize the worn microstructures. It was found that in air at the slow sliding velocity of 0.1 m/s C-doped FeNiMnAlCr exhibited a much lower wear rate of 3.0×10^{-5} mm ³ /N/m compared to either 316 stainless steel (2.9×10^{-4} mm ³ /N/m) or CoCrFeMnNi (3.4×10^{-4} mm ³ /N/m). In contrast, both in argon at this slow sliding velocity and in air at the high sliding velocity of 1.0 m/s, all three material showed similar wear rates of $\sim (2.4 \pm 0.6) \times 10^{-5}$ mm ³ /N/m and $\sim (1.2 \pm 0.3) \times 10^{-5}$ mm ³ /N/m, respectively, indicating the strong effect of the environment and pin tip temperature on the wear rates. The oxide that formed on the C-doped FeNiMnAlCr alloy was found to be more stable and durable than that on either the CoCrFeMnNi or on the 316 stainless steel, and the wear debris from C-doped FeNiMnAlCr had the smallest diameter (3μ m) and the lowest oxygen content of 39 at. %. Greater Al ₂ O ₃ and less Fe ₂ O ₃ , MnO _x or Cr ₂ O ₃ on the worn surface of C-doped FeNiMnAlCr contributed to a peeled-off or delaminated morphology with a higher oxygen content of 46 at. % compared to the worn surfaces of the 316 stainless steel and the CoCrFeMnNi, which both exhibited grooved worn surfaces with lateral cracks and lower oxygen contents of 7.5 at. % and 31 at. %, respectively. The harder Al ₂ O ₃ oxide film was stable and adherent during wear testing and helped protect the worn pin's tip, which was the reason for the increased wear resistance of the C-doped FeNiMnAlCr. The wear protectio

1. Introduction

High entropy alloys (HEAs) are being developed with various properties to satisfy a wide range of applications. For example, FeCoNi- $Cu_{0.2}Si_{0.2}$ and AlCoCrFeNi combine soft magnetic properties and good mechanical properties [1,2], while $Co_{1.5}CrFeNi_{1.5}Ti$ and $Al_{0.2}Co_{1.5}CrFeNi_{1.5}Ti$ have high wear resistance [3]. AlCoCrFeNi, which has a body-

centered-cubic structure (b.c.c.), has very high strength at room temperature, while b.c.c. NbMoTaV has high strength at elevated temperatures [3]. Cu_{0.5}NiAlCoCrFeSi HEA has better corrosion resistance than 304 stainless steel [3]. HEAs are being also considered for their biocompatibility [4]. Many single phase f.c.c. HEAs with good mechanical properties contain substantial proportions of Co, Cr and Ni, such as CoCrFeMnNi [5], (FeCoNiCr)₉4Ti₂Al₄ [6], CoCrFeNiMo_x [7],

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Received 2 June 2020; Received in revised form 14 September 2020; Accepted 6 October 2020 Available online 9 October 2020 1044-5803/© 2020 Elsevier Inc. All rights reserved. and $Al_{0.3}$ CoCrFeNi [8]. The high cost of these elements, particularly Co, limits the wide engineering applications of these HEAs. Thus, several high-performance carbon-doped, single-phase, f.c.c. Co-free Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEAs with lower Ni and Cr contents and, hence, much lower cost have been designed [9,10]. It is well-known that interstitial carbon increases the strength of steel. These interstitials interact strongly with stacking faults between dislocation partials, resulting in serrated flow during tension testing. This effect arises from dynamic strain aging [11]. Such affects are also found in carbon-doped high entropy alloys, where interstitial carbon can produce substantial lattice strains leading to strengthening [9,10,12]. Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ doped with 1.1 at. % carbon has been shown to exhibit both good room temperature yield strength of 355 MPa and 50% elongation in the as-cast condition [10]. Thus far, there have been no published studies of the wear properties of this HEA.

In many cases, the wear rate of materials may be approximated by the Archard law [13,14], i.e.

$$W = K F L/H$$
(1)

where W is the volume loss of materials through wear, K is the wear coefficient, F is the normal load, L is the sliding distance, and H is the hardness of the material. Exceptions to (1) have been noted; for example, a study on NiTi alloys [15] found that the wear resistance anomalously decreased with increasing hardness, resulting from an increase of the austenite elastic modulus and a decrease of the amount of phase transition.

There have been a number of studies on the room temperature wear of several HEAs, which have generally shown good wear resistance [16–19], but no better wear resistance than would be expected of a traditional metallic alloys of similar hardness [20]. However, Tsai and Yeh [20] noted three HEAs that showed exceptional wear resistance compared to commercial alloys of similar hardness, one of which, Co1 5CrFeNi1 5Ti, exhibited a wear resistance comparable to that of H13 tool steel even though the hardness of H13 steel is greater [20]. Kong et al. [21] found that annealed AlCoCrFeNiTi_{0.5} high entropy alloy exhibits better wear resistance than remelted alloy, and was attributed to the more uniform distribution of microstructures and enhanced hardness. Joseph et al. [22] found that wear rates of CoCrFeMnNi and Alx-CoCrFeNi high entropy alloys decreased with increasing temperature, and the wear mechanism changed from abrasive wear at room temperature to oxidative and delamination wear at elevated temperatures. Wang et al. [23] found the contrary results in the (CoCrFeMnNi)₈₅Ti₁₅ high-entropy alloy coating, as the wear resistance increases as temperature rises and the best wear resistance was obtained at 400 $^\circ\text{C},$ and the dominat wear mechnisam is oxidation wear, adhesive wear and contact fatigue.

Sliding contact produces substantial heating during wear tests as frictional energy is dissipated, which results in a local temperature increase [24]. Such a temperature increase can reduce the material's hardness and make plastic deformation at the contact area much easier, and hence the wear rate would also be expected to be greater according to eq. (1) [24]. This temperature increase can also lead to greater oxidation of the contacting surfaces. In iron-based metals, it has been thought that the formation of oxide film on the surface could increase the wear resistance of the base metals [25]. Although an oxide could work as protection of the metallic surface during wear, it may break off to produce third-body wear particles, i.e. abrasive wear debris [26]. When wear tests are performed at a slow speed and limited load, the oxides in iron-based alloys are usually soft and part of the oxide film spalls to produce mild oxidative wear [26]. If the wear debris is much harder than the metal layer, it could lead to severe wear, which has been found in NiAl-based alloys [27]. The influence of oxide films on the wear behavior of high entropy alloys can play an important role in the improvement of wear resistance. Zhu et al. [28] studied the wear behavior of CoCrFeNiMn high-entropy alloys reinforced by TiN-Al₂O₃ particles. Abrasive wear was promoted and adhesive wear was eliminated due to $TiN-Al_2O_3$ particles, which enhanced the hardness and wear resistance of the CoCrFeNiMn coatings.

In the present study, the dry sliding wear behavior of 1.1 at. % carbon-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ alloy pins against an yttriastabilized zirconia (YSZ) disk was studied and compared with the wear behavior of similar tests of pins of both the much-studied equiatomic CoCrFeMnNi and 316 stainless steel. Tests were performed at two sliding speeds of 0.1 m.s⁻¹ and 1.0 m.s⁻¹ in air, and additional tests were run in dry argon at 0.1 m.s⁻¹. A scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometry (EDS) and electron backscattered diffraction (EBSD); X-ray photoelectron spectroscopy (XPS); and atom probe tomography (APT) were used to determine the oxide types and distribution on the worn pins' surfaces and the microstructure of the wear pins in order to illuminate the wear mechanisms.

2. Experimental

The ingot of equi-atomic CoCrFeMnNi alloy was provided by Dr. Easo George at Oak Ridge National Laboratory (ORNL), where it was produced by vacuum induction melting and cast into a cylindrical mold. The ingot of 1.1 at. % carbon-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ alloy was prepared by Min Song from Central South University in China by casting a large ingot (7.5 Kg). Cylindrical wear pins (19 mm long, 9.5 mm dia.) with hemispherical tips were machined from as-cast ingots of 1.1 at. % carbon-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ alloy, equiatomic CoCrFeMnNi and hot-rolled and annealed 316 stainless steel rods. The bulk composition analysis was conducted using an Agilent 5110 Dual View ICP-OES and a Leco CS200 combustion analyzer. The measured compositions are listed in Table 1. The density were measured using the Archimedes method as 7.11 g/cm³, 7.51 g/cm³ and 7.82 g/cm³ for 1.1 at. % carbondoped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ alloy, equiatomic CoCrFeMnNi and 316 stainless steel, respectively. The average grain sizes of the C-doped FeNiMnAlCr and CoCrFeMnNi HEAs were $\sim 400 \ \mu m$, while the average grain size of the hot-rolled and annealed 316 stainless steel was ~ 100 μ m, as confirmed by EBSD results in Fig. 1. It should be noted that 316 stainless steel had a deformed microstructure resulting from the processing, as the colour gradients in Fig. 1b show.

Pin-on-disk wear tests were performed against a zirconia disk of 10 cm diameter containing 2.8 mol% yttria, produced by Saint-Gobain Advanced Ceramics. In order to ensure an average surface roughness (Ra) below 0.05 μ m, all pins were ground with SiC papers from 400, 800 and 1000-grit, then polished in gamma alumina polishing suspensions from 0.3 μ m to 0.05 μ m micron size, and finally dried in a furnace at 120 °C. The YSZ disk was polished to an average surface roughness (Ra) below 0.05 μ m; the disk had a Vickers hardness value of 1339 \pm 50 HV.

The wear tests were performed using a previously-described pin-ondisk test system [27]. A strain gage force transducer on the pin holder allowed continuous measurement of friction forces. Wear tests were performed at 0.1 m/s and 1.0 m/s sliding velocities in air at room temperature, and additional tests at 0.1 m/s in argon at room temperature were also conducted for comparison. The normal load on the pins was 23 N and the sliding distance was 1 km for each test. The temperature and humidity were measured using a SensorPush HT1 wireless hygrometer. The measured relative humidity averaged 32% at 25 °C. Wear debris were collected from the disk using adhesive tape. Wear tests for each condition and for all alloys were repeated three times. The wear rates of the pins were measured by the mass loss of pin specimens after wear tests using a Digital Precision scale lab analytical balance with 0.1 mg precision.

After the wear tests, the surfaces of the worn pins were characterized using a Phase Shift micron XAM optical profilometer, through which the depths of wear grooves of pins were measured. The worn surfaces, crosssections of the worn pins and collected wear debris were analyzed using a FEI Scios2 LoVac dual beam SEM operated at 30 kV equipped with EDAX SDD X-ray detector. Several worn pins were sectioned through the

Measured composition of raw materials (unit at. %).

Materials	Fe	Ni	Mn	Cr	Al	Со	С	Мо	Si	Cu	v	Ν
C-doped FeNiMnAlCr 316 stainless steel CoCrFeMnNi	39.3 67.9 20.2	10.6 10.5 19.5	36.2 1.3 20.2	5.7 17.2 20.9	7.3 - -	- 0.2 19.2	0.9 0.8 -	- 0.9 -	- 0.5 -	- 0.4 -	- 0.1 -	0.2



Fig. 1. EBSD maps of the three as-received materials (a) C-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6C_1$; (b) 316 stainless steel; (c) equi-atomic CoCrFeMnNi; and (d) distribution of grain sizes for the three materials. The legend for the colour code is inserted in (b).

wear scar, then mounted with Duroplast resin. EBSD patterns of the raw materials and cross-sections of pins were used to characterize the degree of plastic deformation in the worn region. The cross sections of worn pin specimens were prepared by embedding them in resin to protect the worn surface. The resin we used is not electrically conductive so as to prevent any charging effect during the sample preparation. The samples for EBSD examination were ground using silicon carbide paper from 400 grit to 1200 grit, and then polished using a 0.3 mm alumina suspension, before finishing in a Vibromet polishing machine using a 60 nm colloidal silica suspension. EBSD patterns could be detected about 10 μ m beneath the surface, as the tip surface of cross section was embedded into resin.

The EBSD patterns were analyzed using OIM 7 software. In order to determine the specific oxides present, XPS measurements were undertaken on the worn surface using a spectrometer (ESCALAB 250; Thermo Fisher Scientific). The atomic distribution of the oxides produced in the worn surface was characterized using APT. A plasma focussed ion beam (PFIB)-SEM system (a prototype ThermoFisher Multigats Helios UX G4 PFIB) was used to prepare needle-shaped APT tips from 1–5 µm below the worn pins' tip following procedures described elsewhere [29,30]. APT measurements were performed using a local electrode atom probe (CAMECA LEAP 4000× HR) with a 50 pJ laser energy, a repetition rate of 200 kHz, and a specimen temperature of 50 K [31]. IVAS 3.8.4 software (CAMECA Instruments) was used to reconstruct and analyze the resulting datasets.

The hardnesses of the raw materials and worn surfaces were measured using a TH713 Vickers hardness tester with 2.94 N load and

15 s loading time according to the American Society for Testing and Materials (ASTM) E384–16 standards [32]. Five indents were made on the surface of samples with spacing more than 2 mm between them. The starting materials were ground and polished to a mirror finish for hardness testing, while hardnesses of the worn surfaces were tested without further preparation after the wear tests.

The volumetric wear rate of the counterface YSZ disks was estimated after each wear test. The average wear rates of the YSZ disk could be calculated as

$$W_V = \pi \cdot D \cdot t \cdot w \tag{2}$$

where W_V is the volumetric wear rate of the wear track on the YSZ disk, the unit is mm³/km; *D* is the average diameter of the wear track on the disk; t is the average depth of wear grooves measured using the Phase Shift micron XAM optical profilometer; *w* is the average width of the wear track. The diameter and width were measured using the micrometer. All the diameter, depth and width of wear grooves were measured more than three times to get the average value of W_V .

3. Results and discussion

The wear rates of the three materials, after sliding under various conditions for 1 km under a load of 23 N against the YSZ disk, are shown in Fig. 2. Error bars signify standard deviations for the three samples per test condition. The C-doped FeNiMnAlCr had a wear rate of 3.0×10^{-5}



Fig. 2. Wear rates of C-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$, 316 stainless steel and equi-atomic CoCrFeMnNi sliding against a YSZ disk at speeds of 0.1 m/s under various conditions, and 1.0 m/s.

mm³/N/m at 0.1 m/s sliding speed in air, which is much lower than those of the 316 stainless steel ($2.9 \times 10^{-4} \text{ mm}^3/\text{N/m}$), and of the CoCrFeMnNi ($3.4 \times 10^{-4} \text{ mm}^3/\text{N/m}$) at the same sliding speed. The wear rate of C-doped FeNiMnAlCr was very similar (within measurement error) when tested in either air or argon at 0.1 m/s. On the other hand, wear rates of 316 stainless steel and CoCrFeMnNi were approximately an order of magnitude lower in argon than in air in tests at 0.1 m/s. The low wear rates for the CoCrFeMnNi and 316 stainless steel materials in argon, compared with their much higher wear rates in air, indicates that the presence of oxygen in the test environment clearly affected the wear behavior of those two materials, particularly in low-speed tests. Interestingly, the wear rates at 1.0 m/s in air were similar for the three materials at 9.2×10^{-6} , 1.1×10^{-5} and $1.5 \times 10^{-5} \text{ mm}^3/$ N/m for C-doped FeNiMnAlCr, 316 stainless steel and CoCrFeMnNi, respectively.

Friction was variable during the tests, but the average measured friction coefficients were not significangly different for the three materials; results are shown in Fig. 3. The friction coefficnts for tests in air at 0.1 m/s were between 0.60 and 0.65 for the three materials, whereas friction was slightly lower (0.52–0.57) during tests run at 1.0 m/s. Despite the variability, there was no significant change in friction over the course of the tests for any material at either test speed (i.e., no significant running-in period). It should be noted that the friction coefficients reported here are consistent with those measured for similar materials in other studies (e.g., [33,34]). Friction coefficients during



Fig. 3. Friction coefficient of C-doped FeNiMnAlCr, 316 stainless steel and equi-atomic CoCrFeMnNi pins against YSZ disk: (a) at 0.1 m/s sliding speed in air; (b) at 1.0 m/s sliding speed in air; (c) at 0.1 m/s sliding speed in argon.

tests in argon differed between the materials being tested; friction for Cdoped FeNiMnAlCr was about the same as when tested in air, for CoCrFeMnNi the friction was slightly lower in argon, for 316 stainless steel the friction was about 10–15% higher in argon.

After the wear tests, the roughnesses and morphologies of the worn pin surfaces were determined using both the SEM and optical profilometry of the worn surfaces; see Fig. 4 and Fig. 5 for 0.1 m/s and 1.0 m/s speeds, respectively. The small worn area size in the secondary electron (SE) images of the C-doped FeNiMnAlCr (see Fig. 4a and 5a) indicated it has the best wear resistance. The light areas on the worn surfaces of 316 stainless steel and CoCrFeMnNi alloys (see Fig. 4c, Fig. 5b and c) were deep wear scars, indicating worse wear resistance. The overall wear groove depth of C-doped FeNiMnAlCr was less than $\sim 1.5 \ \mu m$ (Fig. 4g and 5g), compared with \sim 3 µm for 316 stainless steel (Fig. 4h and 5h) and \sim 5 µm or more for the CoCrFeMnNi alloy (Fig. 4i and 5i). The greater depth of the wear grooves in Figs. 4h, i, and 5i may be indicative of more abrasive wear in those cases. The roughness and morphology of the worn pin surfaces after tests at 0.1 m/s in argon at room temperature are shown in Fig. 6. After being worn in argon, the three materials had essentially the same worn area, as shown in Fig. 6a, b, and c. The depths of wear grooves were all approximately 1 µm, as shown in Fig. 6g, h and i.

SE images of the worn surfaces at higher magnification are shown in

Fig. 7 for pins tested at 0.1 m/s and 1.0 m/s sliding speeds. The compositions of the worn surfaces were obtained from the EDS spectra, see Table 2. For the 0.1 m/s sliding speed, the worn surface of C-doped FeNiMnAlCr has a peeled-off or delaminated morphology (Fig. 7a), with a higher oxygen content of 46 at.% (Table 2). In contrast, the 316 stainless steel and CoCrFeMnNi alloys have grooved worn surfaces with lateral cracks (Fig. 7c and e). The oxygen peak from the 316 stainless steel worn pin is extremely low with 7.5 at.%, whereas the CoCrFeMnNi worn surface has 31 at. % oxygen. These results indicate that there were more oxides on the worn surfaces of C-doped FeNiMnAlCr and CoCr-FeMnNi than on the 316 stainless steel at low sliding speed. Very little zirconium (from the disk) was found on any of the worn surfaces after low speed (0.1 m/s) wear tests.

For 1.0 m/s sliding speed, deep worn pits formed on the worn surfaces. The size of the pits on the C-doped FeNiMnAlCr worn surface (Fig. 7b) was the smallest compared with the other two materials (Fig. 7d and f). EDS results from worn surfaces were quite different from those at the low sliding speed condition. Yttrium and zirconium were present in the spectra, indicating that the YSZ disk had been worn, and that hard zirconia wear debris had transferred to the pin surfaces, contributing to the lower wear rates at 1.0 m/s sliding speed. As shown in Table 2, the zirconium contents were 30 at. %, 1 at. % and 9 at. % for C-doped FeNiMnAlCr, 316 stainless steel and CoCrFeMnNi, respectively.



Fig. 4. Secondary electron and optical profilometry images of worn surfaces after wear tests at 0.1 m/s sliding speed in air against the YSZ disk; The depth of wear grooves is shown under the profilometry images. (a) (d) (g) C-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ (at. %); (b) (e) (h) 316 stainless steel; (c) (f) (i) Equi-atomic CoCrFeMnNi. The sliding direction is shown by red or black arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Secondary electron and optical profilometry images of worn surfaces after wear tests at 1.0 m/s sliding speed in air against the YSZ disk; The depth of wear grooves is shown under the profilometry images. (a) (d) (g) C-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ (at. %); (b) (e) (h) 316 stainless steel; (c) (f) (i) Equi-atomic CoCrFeMnNi. The sliding direction is shown by red or black arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This indicates that there was more zirconia on the C-doped FeNiMnAlCr worn surface, enhancing the superior wear resistance of this material.

Wear debris were collected and characterized using an SEM and EDS, as shown in Fig. 8 for 0.1 m/s and 1.0 m/s sliding speeds. The compositions of wear debris were obtained from the EDS spectra, see Table 3. The size of wear debris was measured, and the average diameters are shown in Fig. 9. For the 0.1 m/s sliding speed, wear debris from C-doped FeNiMnAlCr had a smaller average diameter (2.9 μ m) and lower oxygen content of 39 at. % compared with 4 μm and 44 at. % for CoCrFeMnNi which had an average particle diameter of 6 µm. Debris with size of 4 µm and even lower oxygen content of 26 wt% appeared from 316 stainless steel. Since there was very little zirconium in the debris, the oxygen must have come from oxides formed during wear tests. Comparing the oxygen contents found in the wear debris (Table 3) with the oxygen content results on the worn surface (Table 2), it is apparent that oxides that formed on the C-doped FeNiMnAlCr alloy pin surface tended to be more stable and adherent, and therefore more protective, than those on the CoCrFeMnNi or 316 stainless steel surfaces. The oxides on worn CoCr-FeMnNi alloy surfaces broke off into large pieces of average size 6 µm, contributing to the deepest wear groove and highest wear rate.

For 1.0 m/s sliding speed, the EDS results showed that the main content of the wear debris was zirconium and yttrium, indicating that much of the debris had originated on the YSZ disk, in agreement with the EDS results on the worn surfaces. The smaller average wear particle diameter of 5 μ m from the worn C-doped FeNiMnAlCr pins at 1.0 m/s

indicated the abrasion process was milder than for the 316 stainless steel with $6 \mu m$ debris and CoCrFeMnNi with $12 \mu m$ debris.

The wear behaviors of the two HEAs were significantly different. EDS results from worn surfaces and debris indicated that the oxides formed on C-doped FeNiMnAlCr surfaces were more stable and adherent, which resulted in smaller debris and milder abrasion by the third-body debris. In order to understand the role of oxides on wear behavior of these high entropy alloys, XPS was used to quantitatively analyze the oxide types and their relative amount. XPS results from the C-doped FeNiMnAlCr and CoCrFeMnNi worn surfaces after wear tests at 0.1 m/s speed are compared using Fe, Ni, Cr, Mn, Co and Al 2p spectra, as shown in Fig. 10. XPS peaks were fitted and compared with the NIST database [35]. For both of the alloys, the Fe 2p ionization shows two peaks representing a single constituent of Fe_2O_3 (711.5 eV of $2p_{3/2}$ and 724.4 eV of $2p_{1/2}$), while the Ni 2p ionization exhibits two main peaks with two satellite peaks, representing a single constituent of NiO (855.1 eV of 2p3/2, 861.2 eV of $2p_{3/2, sat}$, 873.2 eV of $2p_{1/2}$ and 879.5 eV of $2p_{1/2, sat}$), as shown in Fig. 10a and b.

The Cr 2p spectra obtained from the worn HEA pin surfaces are shown in Fig. 10c. The spectrum from C-doped FeNiMnAlCr worn surface is separated into several constituent peaks representing metallic Cr (573.2 eV of $2p_{3/2}$), CrO₃ (578.7 eV of $2p_{3/2}$) and Cr₂O₃ (576.8 eV of $2p_{3/2}$, 586.7 eV of $2p_{1/2}$), while a single Cr₂O₃ constituent appeared in the spectrum of the CoCrFeMnNi worn surface. The result of the Cr-2p spectra indicates that metallic Cr in C-doped FeNiMnAlCr didn't fully



Fig. 6. Secondary electron and optical profilometry images of worn surfaces after wear tests at 0.1 m/s sliding speed in argon against the YSZ disk; The depth of wear grooves is shown under the profilometry images. (a) (d) (g) C-doped $Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr_6$ (at. %); (b) (e) (h) 316 stainless steel; (c) (f) (i) Equi-atomic CoCrFeMnNi. The sliding direction is shown by red or black arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxidize during the wear tests at 0.1 m/s, in contrast to the CoCrFeMnNi specimens. As shown in Fig. 10d, the constituent peaks of Mn₂O₃, Mn₃O₄ and MnO overlap with each other in the Mn 2p spectrum for both alloys. Note that there was an extra constituent peak of Mn_2O_7 (646.7 eV of $2p_{3/2}$ $_{\rm 2})$ that appeared on the worn surface of CoCrFeMnNi, but this $\rm Mn_2O_7$ is an unstable form and the detected peak was probably from a permanganate. The Co 2p spectra on worn surface of CoCrFeMnNi, as shown in Fig. 10e, indicated single constituent of Co₂O₃ (781.1 eV of 2p_{3/2}, 786.3 eV of $2p_{3/2, sat}$, 797.2 eV of $2p_{1/2}$ and 803.9 eV of $2p_{1/2, sat}$) was produced. For the Al 2p spectrum on the worn surface of C-doped FeNiMnAlCr, peaks of NiO (67.7 eV of 3p) and Al₂O₃ (74 eV of 2p_{3/2} and 77 eV of 2p3/2, sat) appeared, as shown in Fig. 10f. The fractions of oxides on the worn surface were calculated from fitting areas in Fig. 10 according to Eq. (3) [36] and are listed in Table 4. CA represents the surface composition of the sample for element A, in atomic %; IA is the fitting area of each constituent $2p_{3/2}$ peak for element A; S_A is the response factor associated with element A, which is given by the XPS instrument. The values of S were 16.42 for Fe, 22.18 for Ni, 13.91 for Mn, 11.67 of Cr, 19.16 for Co and 0.537 for Al.

$$C_A = \left(\frac{I_A}{S_A}\right) \left/ \sum_i \left(\frac{I_i}{S_i}\right) \right. \tag{3}$$

The main oxides on the worn surface of C-doped FeNiMnAlCr were 43% Al_2O_3 , 17% Fe_2O_3 and 18% MnO_x , compared with 37% Fe_2O_3 , 36% MnOx and 12% Cr_2O_3 on worn CoCrFeMnNi surfaces.

To unmask the protection mechanism of these three different

materials, we utilized atom probe tomography to visualize the elemental distribution at the nanoscale in needle-shaped APT tips after wear tests at 1.0 m/s sliding speed. The tops of the APT tips were very close to the worn surface (about 1 μ m below the surface) and the bottoms of the tips were about 5 μm beneath the surface. Therefore, the APT tips enabled analysis of the near-surface regions of the worn tips. Fig. 11a shows the 3D atomic distribution maps of Fe, Cr, Mn, Ni, Al, and AlO in the Cdoped FeNiMnAlCr wear pin. Oxygen-rich regions can be seen at several depths within the worn pin specimen. The proxigram (Fig. 11b) based on one of the 3 at.% O isoconcentration surfaces clearly reveals the matrix region with base metal composition and adjoining O-rich regions containing multiple metal elements (complex metal oxides). Those O-rich regions contain both individual particles and continuous networks. Cr and C appear to be enriched in the O-rich region, while Al, Ni, Mn, and Fe are depleted in the O-rich region. It is striking to observe that Al atoms tend to segregate within the O-rich region, being concentrated closest to the interface with the matrix region. Fig. 11c shows the 3D atomic distribution maps of Fe, Cr, Mn, Ni, CrO, and CrO2 in the 316 stainless steel wear pin. Again, multiple O-rich regions are scattered throughout the near-surface depth of the worn pin. The proxigram (Fig. 11d) based on a 13 at.% O isoconcentration region clearly reveals the matrix region with base metal elements and the O-rich region containing multiple metal elements (complex metal oxides). Cr and Mn are seen to be enriched in the O-rich region, while Fe and Ni are depleted in the O-rich region. No segregate behavior was found in the O-rich region near the interfaces between the matrix region and the O-rich region. Fig. 11e shows the 3D atomic distribution maps of Fe, Cr, Mn, Ni, Co,



Fig. 7. Secondary electron images of worn surfaces of three materials after wear tests at different sliding speeds against the YSZ disk: C-doped $Fe_{40.4}Ni_{11.3}M-n_{34.8}Al_{7.5}Cr_6$ (at. %) at (a) 0.1 m/s and (b) 1.0 m/s; 316 stainless steel at (c) 0.1 m/s and (d) 1.0 m/s; Equi-atomic CoCrFeMnNi at (e) 0.1 m/s and (f) 1.0 m/s. The sliding direction is shown by red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The composition from EDS analysis of worn pins' surface (unit at. %).

Materials	Speeds	Fe	Ni	Mn	Cr	Al	Со	0	Zr	Y
	0.1 m/s	21.3	5 5	10.2	3.4	43	_	46.3		
C-doped FeNiMnAlCr	1.0 m/s	1.5	0.8	1.3	-	-	_	63.6	30.3	2.5
216 staiplass staal	0.1 m/s	63.2	8.9	1.3	19.1	-	-	7.5	-	-
310 stanless steel	1.0 m/s	41.8	6.3	1.4	11.9	-	-	37.5	1.1	-
CoCrEeMpNi	0.1 m/s	14.1	12.8	13.9	14.9	-	13.3	31.0	-	-
Cociremina	1.0 m/s	17.0	14.7	14.9	16.8	-	16.4	11.2	9.0	-

CrO and CrO₂ in the worn CoCrFeMnNi pin, and again many O-rich regions are seen among regions of metal matrix. The proxigram (Fig. 11f) based on the 3 at.% O isoconcentration surfaces clearly reveals the matrix region with base metal elements and the O-rich region with multiple metal elements (complex metal oxides). Similar to the partitioning behavior in 316 stainless steel, Cr and Mn appear to be enriched in the O-rich region, while Fe, Co and Ni are depleted in the O-rich region. No segregate behavior was found near the interfaces between the matrix region and the O-rich region.

By comparing APT results, we can conclude that oxides were found throughout the mechanically-mixed near-surface region of worn pins of all three materials after tests at 1.0 m/s, but fewer oxides were found in the top few microns of the worn C-doped FeNiMnAlCr compared with the other two alloys. Al atoms tended to segregate in the O-rich region of the worn C-doped FeNiMnAlCr alloy pins, with highest concentration near the interface between the O-rich region and the matrix region. It can also be noted that no zirconium appeared in the subsurface APT results shown in Fig. 11. Evidently the transferred zirconia wear debris produced during tests at 1.0 m/s remained on the worn pin surfaces, as was shown in Table 2, but the zirconia particles did not get mixed into the subsurface regions of the worn pins. In addition, the APT results in Fig. 11 showed no evidence of carbides in the region beneath the worn surface for any of the tested materials.

XPS and APT results indicate that the better wear resistance of C-



Fig. 8. Secondary electron images of collected wear debris from three materials after wear tests at 0.1 m/s sliding speed against the YSZ disk: C-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ (at. %) at (a) 0.1 m/s and (b) 1.0 m/s; 316 stainless steel at (c) 0.1 m/s and (d)1.0 m/s; Equi-atomic CoCrFeMnNi at (e) 0.1 m/s and (f) 1.0 m/s.

The composition from	EDS analysis of	f wear debris	(unit at. %	b)
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	Materials	Speeds	Fe	Ni	Mn	Cr	Al	Со	0	Zr	Y	С
Ī	C-doped FeNiMnAlCr	0.1 m/s	22.4	5.1	18.8	3.3	3.2	_	39.4	0.3	-	7.5
		1.0 m/s	2.0	1.1	1.6	0.2	-	-	58.5	33.4	0.5	2.7
	316 stainless steel	0.1 m/s	42.1	5.7	1.0	11.8	-	-	25.8	0.3	-	13.3
		1.0 m/s	0.7	-	-	0.5	-	-	64.6	25.5	-	8.7
	CoCrFeMnNi	0.1 m/s	7.0	6.6	6.6	6.8	-	6.5	43.9	-	_	22.6
		1.0 m/s	0.4	0.3	0.4	0.5	-	0.3	63.3	33.4	1.4	-

doped FeNiMnAlCr at low sliding speeds can be attributed to a greater accumulation of Al_2O_3 on and, to a lesser extent, mixed within the thin mechanically-mixed layer beneath the worn surface of the material. Smaller amounts of Fe₂O₃, MnOx or Cr₂O₃ constituents appeared on the worn surface and in the near surface regions, where they were less segregated than the aluminum oxide.

The four kinds of oxides present, i.e. Al_2O_3 , Fe_2O_3 , MnO_x and Cr_2O_3 , have different hardness values [37–39]. Al_2O_3 has the highest Vickers hardness of 2600 HV [37]. Fe_2O_3 with 300 HV [38] and MnOx with 630 to 743 HV [39] are softer oxides on the worn surface. Note that the value of Cr_2O_3 is 2955 HV [37], which is close to that of Al_2O_3 . The Vickers hardness of the YSZ disk is 1339 HV, which is softer than the Al_2O_3 . With more Al_2O_3 on the worn surface of C-doped FeNiMnAlCr, the oxide particles could act as abrasive third bodies to wear the YSZ disk, thus protecting the metal base, and producing a worn surface that was much smoother (as shown in Fig. 4d and 7a). The removed wear debris would have smaller size and less oxygen content as the Al_2O_3 particles are hard enough to resist the plastic deformation and fracture induced from friction; therefore, much of the wear debris would be from softer oxides and substrate material, as shown in Fig. 8a.

With more soft oxides on the worn surface of CoCrFeMnNi, the oxide film formed on that material during sliding could be removed more easily. The removed oxide particles resulted in larger wear debris with higher oxide contents, as shown in the wear debris results for CoCr-FeMnNi in Fig. 8e. It should be noted that a recent study by Ayyagari et al. [33] also found considerable wear of CoCrFeMnNi during dry



Fig. 9. The average diameter of collected wear debris particles of the three materials after wear tests at 0.1 m/s and 1.0 m/s sliding speeds against a YSZ disk.

reciprocating sliding at low speed (about 0.04 m/s). They attributed the high wear rate to adhesive pullout of material at work-hardened junctions in the base material, but they did not investigate the presence or absence of oxides on the worn surfaces or in the wear debris or any influence of oxides on wear. Based on the results of this study, it appears likely that oxide formation and removal may have also played a role in wear groove formation in the work reported in [33].

The hardnesses of the worn surfaces were tested and compared with the raw materials to understand the protective role of the different oxides, as shown in Fig. 12. After sliding tests at 0.1 m/s, the hardness of the C-doped FeNiMnAlCr surfaces increased dramatically from 140 HV of the raw material to 390 HV of the worn surface, compared with the 142 HV to 270 HV for the CoCrFeMnNi specimens. The hardness results for the two HEAs agree well with the discussion of the contribution of the different oxides to the hardness. The hardness of worn surfaces of the two HEAs after wear tests at 1.0 m/s was significantly influenced by the transfer of zirconia from the YSZ disk, which was shown in the EDS results of worn surface and wear debris (Table 2 and Table 3). Thus, there was less difference between the two alloys (438 HV for C-doped FeNiMnAlCr compared with 424 HV for CoCrFeMnNi). As a result, the harder surfaces of both HEA materials after the higher speed tests made the two materals more resistant to wear by both abrasion and deformation-related wear mechanisms, e.g., delamination. There was not much zirconia on the worn surface of 316 stainless steel after sliding at 1.0 m/s. In contrast to the cast HEAs, the 316 stainless steel exhibits a deformed microstructure, and as a result it shows a relatively high initial hardness due to stain hardening. According to Archard's law (1), it might be expected that the higher initial hardness of 316 stainless steel should provide it with better wear resistance, but that didn't necessarily occur, particularly in the low speed sliding tests. In fact, the hardness of the worn 316 stainless steel surface ended up being essentially the same as that of the worn C-doped FeNiMnAlCr after tests at both sliding speeds.

It has long been known that changes in the surface and near-surface hardness can occur during sliding contact as a result of processe such as plastic deformation, phase transformation, mechanical mixing and oxidation [40]. Ji et al. [41] introduced a relationship between wear resistance, w, and the surface hardness, H_w , i.e.

$$w = 2.539 \times \left(1000 * \frac{H_w}{E}\right) - 1.020$$
 (4)

where E is the elastic modulus. In order to calculate *w* from Eq. (4), the hardness on the worn surface in this study was used for H_w. The elastic modulus of 1.1 at. % C-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ is 140 GPa [10], 195 GPa for 316 stainless steel [42], and 203 GPa for CoCrFeMnNi [43]. After sliding tests at 0.1 m/s, C-doped FeNiMnAlCr has the highest H_w/E value of 0.028 compared with the 0.021 for 316 stainless steel, and only 0.013 for CoCrFeMnNi. At 1.0 m/s, the Hw/E value increased to 0.031 for C-doped FeNiMnAlCr, remained at 0.021 for the 316 stainless steel, and increased to 0.021 for CoCrFeMnNi. Since the wear resistance increases with increasing H_w/E, these calculations also indicate the Cdoped FeNiMnAlCr has the highest wear resistance. The specific wear rates were compared with the change trend of the reciprocal of hardness from raw materials and worn surfaces, as shown in Fig. 13. The H_w represents the hardness from worn surfaces, and H_{raw} represents the hardness of raw materials. It could be seen, in the same change scale, the hardness from the worn surface could represent the wear resistance better.

As reported in the literature [44], with increasing Al content the wear mechanism of high-entropy alloys becomes predominantly oxidative wear. That conclusion appears to be borne out by the results of our study. The large improvement of wear resistance for the C-doped FeNiMnAlCr is primarily because of the oxide (particularly Al₂O₃) and the consequent increased surface hardness which resists plastic deformation. The grain structures on cross-sections of worn pins from three materials after tests at 1.0 m/s sliding speed were obtained by EBSD to characterize the plastic deformation during abrasion. The results are shown in Fig. 14. Severe plastic deformation occurred on the tip of the 316 stainless steel pins (Fig. 14b), with minor deformation bands appearing along the friction direction. Deformed and work-hardened grains, along with the chromium oxides mixed in with those grains (Fig. 11c,d), resulted in higher hardness on and beneath the worn surface of 316 stainless steel, as discussed earlier. There was less plastic deformation in C-doped FeNiMnAlCr (Fig. 14a), as the large grains remained intact, but the surface showed evidence of some significant plastic shearing. The worn tips of CoCrFeMnNi pins were rougher than worn C-doped FeNiMnAlCr pin surfaces, with many unidentified oxides (observed as black areas), as shown in Fig. 14c. There is some small colour change near the surface of the CoCrFeMnNi pins indicating some local plastic deformation, which is unlike more widespread surface deformation of the C-doped FeNiMnAlCr. Instead of plastic deformation at the surface of the CoCrFeMnNi, it appears that material has simply fractured off the surface. This is consistent with Fig. 5, where there is evidence of fracture for CoCrFeMnNi but of plastic flow for C-doped FeNiMnAlCr. The APT results in Fig. 11e,f indicated that the oxides of CoCrFeMnNi were distributed deeply inside the worn surface, which corresponds to the detected black areas in the EBSD characterization. In comparison with C-doped FeNiMnAlCr, there was less surface protection from oxides in the CoCrFeMnNi due to the softer oxides, and these soft oxide films could break off to become wear debris or could be mechanically mixed within the grains.

In many dry sliding situations, the oxidation that occurs on the contacting surfaces is caused by increased surface temperatures resulting from frictional heating at the contact interface [25,26]. Research on medium-entropy CoCrFeNi alloys [45,46] indicated that friction-induced oxidation was increased by testing at high temperatures since the oxygen content of the worn surfaces increased with increasing test temperature. The smooth and complete glaze layer formed on the worn surface, which was also observed in this work on the worn surface of CoCrFeMnNi at 1.0 m/s (Fig. 7f), would reduce the friction coefficient and improve the wear resistance, as confirmed in Zhang et al.'s work [46].

To determine whether the pin tip tempertures in the cases in this work were sufficient to cause oxidation of the type seen here, approximation of the contact temperatures was performed using analytical methodology described in earlier papers [34,47]. The parameters used



Fig. 10. X-ray photoelectron spectroscopy from the worn surface of C-doped FeNiMnAlCr and CoCrFeMnNi after wear tests at 0.1 m/s against YSZ in air; (a) Fe-2p spectra; (b) Ni-2p spectra; (c) Cr-2p spectra; (d) Mn-2p spectra; (e) Co-2p spectra; (f) Al-2p spectra.

The atomic proportion of each oxide on the worn surfaces of C-doped FeNiMnAlCr and CoCrFeMnNi after wear tests at 0.1 m/s sliding speed. The results were calculated from fitting the XPS spectra in Fig. 10.

Oxides types	Fe ₂ O ₃	NiO	Mn _x O _y	Cr	Cr ₂ O ₃	CrO ₃	Al ₂ O ₃	Co_2O_3
FeNiMnAlCr-C	0.17	0.06	0.18	0.06	0.07	0.03	0.43	-
CoCrFeMnNi	0.37	0.08	0.36	-	0.12	-	-	0.07

in the analysis included the elastic and thermal properties of the pin and disk materials, operating conditions (normal load, sliding velocity), and measured friction coefficients. It was found that pin tip temperatures during low speed (0.1 m/s) sliding ranged in magnitude from approximately 300–400 °C. Those temperatures are considered to be sufficient to cause slow oxidation of the pin tip materials [47]. Tests at high speed (1.0 m/s) produced much higher pin tip temperatures, with magnitudes ranging approximately from 1400 to 1500 °C. Temperatures of that magnitude are certainly sufficient to cause rapid oxidation of the pin

materials, and in addition they can cause temperature- and contact stress-induced phase transformation of the zirconia disk material [48]. This transformation from cubic to tetragonal phase can cause localized thermal expansion and cracking of the YSZ disk surface, along with pullout of zirconia grains [48], such as were seen in the wear debris and worn surfaces in these tests.

After each wear test, the volumetric wear rate of the counterface YSZ disk was determined using eq. (2). The results for tests run at a sliding speed of 0.1 m/s in air or argon environment are given in Table 5. It can



Fig. 11. Atom probe results showed the 3D atomic distribution maps of elements and oxygen isoconcentration surfaces, and the corresponding proxigram from the worn surfaces of pins after wear tests at 1.0 m/s. (a) (b) C-doped FeNiMnAlCr; (c) (d) 316 stainless steel; (e) (f) CoCrFeMnNi.

be seen that the YSZ disks suffered greater wear during tests run in argon than in air. The difference was most notable for pins made of the HEA materials, particularly CoCrFeMnNi. Wear of the yttria-stabilized zirconia material, which had a hardness of about 1340 HV, could have occurred by several mechanisms. Harder oxides, such as Al_2O_3 or Cr_2O_3 that were found on the HEA pin surfaces after tests done in air, could abrade the zirconia surface. In addition, frictional heating and contact stress could cause phase transformation of the YSZ material, resulting in pull-out of YSZ grains, as noted above. This latter mechanism appears to



Fig. 12. Vickers hardness of as-received materials compared with hardness of the worn surfaces after wear tests at 0.1 m/s and 1.0 m/s speeds in air.



Fig. 13. The specific wear rates vs the reciprocal of hardness from as-received materials and worn surfaces after wear tests at 0.1 m/s and 1.0 m/s speeds in air.

have been dominant in the argon test environment where few oxides were present. The pulled-out YSZ grains could then transfer to the pin surfaces, resulting in increased surface hardness and wear resistance of the pin materials in the argon test environment. The weight loss of the pins in the argon environment came mainly from the mild two-body abrasion and adhesive (e.g., delamination) wear of the hardened base metal surfaces.

4. Summary

The dry sliding performance of a novel 1.1 at. % C-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ HEA was studied and compared with the behavior of both 316 stainless steel and the f.c.c. equiatomic CoCr-FeMnNi HEA at two different sliding velocities in air, and in argon at a slow sliding rate. Pins of the three materials were slide against yttria-stabilized zirconia disks. EDS, XPS and APT analysis results of oxide types and distribution indicated that there were different protection mechanisms in different alloys. The main conclusions are:

1. In air, at the slow sliding velocity of 0.1 m/s C-doped FeNiMnAlCr showed a much lower wear rate in air of $3.0 \times 10^{-5} \text{ mm}^3/\text{N/m}$ compared to either 316 stainless steel ($2.9 \times 10^{-4} \text{ mm}^3/\text{N/m}$) or CoCrFeMnNi ($3.4 \times 10^{-4} \text{ mm}^3/\text{N/m}$). In contrast, in argon at this



Fig. 14. EBSD maps of cross-sections of worn tips from three materials after tests at 1.0 m/s sliding speed: (a) C-doped Fe_{40.4}Ni_{11.3}Mn_{34.8}Al_{7.5}Cr₆ (at. %); (b) 316 stainless steel; (c) Equi-atomic CoCrFeMnNi; (d) The legend for the colour code and crystal system. The sliding direction is shown by red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The volumetric wear rate of the counterface YSZ disk for tests run at a sliding speed of 0.1 m/s in air or argon environment. The units for wear rates are mm³/N/m. The data are the mean value of three measurements for each test condition.

Materials	Atmosphere	Volumetric wear rate (*10 ⁻⁵ mm ³ /N/m)
C-doped FeNiMnAlCr	Air	6.1 ± 0.4
	Argon	14.8 ± 0.9
216 stainlass staal	Air	6.5 ± 0.9
510 stanness steer	Argon	9.1 ± 1.3
CoCrEoMaNi	Air	$\textbf{4.8} \pm \textbf{0.4}$
COCITEMINI	Argon	13.5 ± 1.3

slow sliding velocity, all three material showed similar wear rates, \sim (2.4 \pm 0.6) \times 10⁻⁵ mm³/N/m, indicating the strong effect of the environment on the wear rates.

- 2. In air, at the high sliding velocity of 1.0 m/s, all three material showed low wear rates, i.e. $9.2 \times 10^{-6} \text{ mm}^3/\text{N/m}$ for C-doped FeNiMnAlCr; $1.1 \times 10^{-5} \text{ mm}^3/\text{N/m}$ for 316 stainless steel; and $1.5 \times 10^{-5} \text{ mm}^3/\text{N/m}$ for CoCrFeMnNi, indicating the strong effect of the pin tip temperature in air on the wear rates.
- 3. For 0.1 m/s sliding speed tests, the worn surface of C-doped FeNiMnAlCr showed a peeled- off or delaminated morphology, with a high oxygen content of 46 at. %. The 316 stainless steel and CoCrFeMnNi had grooved worn surfaces with lateral cracks and lower oxygen content of 7.5 at. % and 31 at. %, respectively.
- 4. For 1.0 m/s sliding speed tests, considerable zirconia content was found on the worn surfaces of all three materials. The zirconia grains had probably been removed from the YSZ disk surface because of contact temperature-induced phase transformation of the zirconia. The C-doped FeNiMnAlCr worn surface contained the largest amount of zirconia, and this resulted in that material having the best wear resistance of the three materials tested.
- 5. Considerable amounts of oxides were found throughout the mechanically-mixed near-surface region of worn pins of all three materials after tests at 1.0 m/s, but fewer oxides were found in the top few microns of the worn C-doped FeNiMnAlCr compared with the other two alloys.
- 6. The wear mechanism of the C-doped FeNiMnAlCr alloy in air is predominantly oxidational wear. The greater wear resistance of Cdoped FeNiMnAlCr is due to both the protective oxide (particularly

 $\rm Al_2O_3)$ that forms on the worn surface and the increased hardness of the near-surface layer containing intermixed hard oxides.

7. The increased wear resistance of the HEA materials in an argon environment can be attributed to the presence of hard zirconia particles from the YSZ counterface disk that transferred to the surface of the worn pins, resulting in a harder, more wear-resistant surface layer. A similar effect appears to have occurred for all three test materials during sliding tests at high sliding speed.

Declaration of Competing Interest

None

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