

Tuning the near room temperature oxidation behavior of highentropy alloy nanoparticles

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ABSTRACT

Understanding the oxidation behavior of high-entropy alloys (HEAs) is essential to their practical applications. Here we conducted *in situ* environmental transmission electron microscopy (E-TEM) observations of dynamic oxidation processes in CrMnFeCoNi and CrFeCoNiPd nanoparticles (NPs) near room temperature. During the oxidation of CrMnFeCoNi NPs, a favorable oxidation product was $MnCr_2O_4$ with the spinel structure. The surface nanoislands of $MnCr_2O_4$ underwent dynamic reconstruction, resulting in the thickened oxide layer with less crystallinity. In CrFeCoNiPd NPs, the reactive element Mn was replaced by the inert element Pd. As a result, a favorable oxide product was CrO_2 with the rutile structure. CrO_2 formed on the NP surface and was a result of Cr outward diffusion through the oxide layer. In addition, FeO nanocrystals formed at the oxide/metal interface and were a result of O inward diffusion through the oxide layer. We also performed first principles calculations to provide insights into the energetics and diffusion rates related to oxide formation. These results reveal the non-equilibrium processes of oxidation in HEA NPs that can be strongly influenced by small particle sizes and large surface areas. This work underscores the high tunability of oxidation behavior in nanoscale HEAs by changing their constituent alloying elements.

KEYWORDS

In situ transmission electron microscopy (TEM), high-entropy alloy (HEA) nanoparticles (NPs), oxidation

1 Introduction

Oxidation can either provide protection to a material through formation of a dense oxide film that resists further corrosive attack or cause degradation of material's structure and properties [1-3]. Alloys have more intricate oxidation characteristics than pure metals owing to the different affinities between oxygen and various alloying elements, diverse formation energies of multiple oxide phases, and varying diffusivities of different elements in both the oxide and alloy [4-6]. High-entropy alloys (HEAs) represent a new class of metallic materials with multi-principal elements and they have recently attracted considerable attention due to the potential of achieving superior mechanical properties, thermal stability, and favorable corrosion resistance [7-10]. Many of these properties of HEAs, especially oxidation resistance, are directly related to the cooperative and/or competitive nature of multiple principal elements [11]. Compared with traditional alloys that have just one or two principal elements, the random solid solution of multiple principal elements in HEA can result in a variety of local chemical environment, which can give rise to many unconventional structures and properties from different combinations of elements [12-14]. Certain elements in HEAs deserve special attention because their individual or collective responses can make a large impact on the oxidation process. In the CrMnFeCoNi-related systems, it has been found that Cr and Mn elements have a significant influence on their oxidation behavior [15, 16]. CrMnFeCoNi experiences a more rapid oxidation process than CoCrFeNi because of the presence of reactive Mn in the former, but it has lower oxidation rates and less scale spallation than CoFeMnNi due to the lack of Cr in the latter [17]. Most previous studies of HEA oxidation have been based on the post-mortem structure characterization of bulk samples at the micro- and submicroscale [18, 19]. Recently, Song et al. performed in situ observations of Fe0.28Co0.21Ni0.20Cu0.08Pt0.23 HEA nanoparticles (NPs). Both the outward diffusion of transition metal elements and the formation of disordered oxide layers are monitored in real time using environmental transmission electron microscopy (E-TEM) [20]. However, the real-time atomic-level oxidation behavior, particularly regarding the interaction of different elements during oxidation, remains largely unexplored, and should be revealed in order to achieve a fundamental understanding of the oxidation mechanism of HEAs.

In this study, we used aberration-corrected E-TEM to conduct *in situ* oxidation observations of CrMnFeCoNi and CrFeCoNiPd HEA NPs. The *in situ* oxidation responses of the NPs were compared with those from their bulk counterparts. Density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations were performed to shed light onto the experimental findings. The combined experimental and

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simulation results provide insights into the effects of different elements on the oxide formation and diffusion process during oxidation of complex multi-principal element alloys.

2 Experimental

2.1 Alloy processing

HEA NPs were synthesized by fast-moving bed pyrolysis as described in a previous study [21] and they were stored in a glovebox under an argon environment. The bulk HEA samples were processed by arc-melting of pure metals (> 99.9% purity) as previously reported [14].

2.2 *In situ* transmission electron microscopy (TEM) observations of oxidation

We prepared *in situ* TEM samples by dispersing the NPs in ethanol. Then we dropped the solution of NPs onto a heating microchip. *In situ* oxidation experiments were performed using aberration-corrected E-TEM (FEI TITAN E-TEM G2: an ultra-high point resolution of 0.1 nm with a Gatan Model-994 CCD digital camera), operated at 300 kV. The dose rate for observation was approximately 7×10^5 e/(nm²·s) to diminish the effects of electron beam. An oxygen environment with a constant pressure of 5×10^{-3} mbar was maintained throughout the experiment. Temperature was ramped up from room temperature (RT) to 50 °C with an increment of 5 °C per minute and then ramped down to RT after *in situ* observation by 50 min at 50 °C.

2.3 Characterization methods

Scanning transmission electron microscopy (STEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analysis were undertaken on a spherical aberration-corrected (Cs-corrected) FEI 80–200 Titan G2 TE microscope, operated at 200 kV, equipped with a large-solid-angle EDS, a high-angle annular dark field (HAADF) detector, and an annular dark field detector. TEM sample of the bulk HEAs were prepared using an FEI Quanta three-dimensional (3D) FEG focused ion beam (FIB) micro-machining technique by Ga⁺ ion beam.

2.4 DFT calculation

DFT calculations of CrMnFeCoNi and CrFeCoNiPd alloys were performed using the Vienna ab initio simulation package (VSAP) [22, 23]. Each alloy configuration contained 180 atoms in a cubic box with periodic boundary conditions and was generated as a special quasi-random structure [24]. Projector-augmentedwave (PAW) [23] potentials were employed with the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [25] for the exchange-correlation function. The wave functions were sampled using a $3 \times 3 \times 3$ k-point [26], and all calculations were performed with spin polarization. The energies of three oxides, CrO₂, FeO, and MnCr₂O₄, were obtained with DFT calculations using the PBE form of GGA + U [27] for the exchange-correlation functional. The crystal structures of the three oxides were established via electron microscopy characterization. The calibrated U values for Cr, Fe, and Mn were chosen as 3.7, 5.3, and 3.9 eV, respectively [27]. An energy cutoff of 520 eV and appropriate k-point meshes were chosen so that the total ground-state energies converged within 3 meV per formula unit. All atomic coordinates and supercell geometries were fully relaxed for each structure.

2.5 AIMD simulation

AIMD simulations were performed at 1,500 K with a fixed

supercell volume, and the temperature was controlled by the nose-Hoover thermostat. The energy cutoff of 300 eV was used with a single *k*-point (Γ). Spin polarization was not included, considering that the studied temperature in this experiment was much higher than the Curie temperatures of the two HEAs studied in this work [28]. A vacancy was randomly introduced at one of the lattice sites for the simulation of vacancy diffusion. A defect structure was first equilibrated by 3 ps, and the diffusion data were then collected from the subsequent AIMD simulation by 40 ps.

3 Results and discussion

Both the CrMnFeCoNi and CrFeCoNiPd NPs were single-phase solid solutions before in situ oxidation experiments. Their structures were characterized in detail in a previous study [21]. The surface of as-prepared nanoparticles was quite clean as shown in Fig. S1 in the Electronic Supplementary Material (ESM). As oxygen flowed in, a thin layer (~ 5 nm thick) of amorphous oxide quickly formed to cover the surface of the NPs. Further growth of the amorphous oxide layer was not obvious. Since the initial amorphous oxide formed through surface atoms in close contact with environmental oxygen atoms, less diffusion was needed. However, the amorphous oxide layer might hinder the diffusion of atoms both inward and outward, slowing down further oxidation. Figure 1 shows a typical CrMnFeCoNi NP of ~ 60 nm in diameter. To facilitate in situ observations within a reasonable time frame, we conducted oxidation experiments at an elevated temperature of ~ 50 °C with low pressure (5 \times 10⁻³ mbar) of O₂. As seen in Fig. 1(a), there were obvious changes in the morphology and element distribution of the CrMnFeCoNi NP after oxidation. The contrast of the whole NP became inhomogeneous, with lighter contrast in its lower part, which corresponds with a newly formed oxide region according to the EDS mapping of O. All the metallic elements were present in this region, except for Ni. However, the overwhelming majority of Cr and Mn overlapped with each other in this oxidized region adjacent to the parent NP, indicating their high diffusion rate and strong correlation. By contrast, all the alloy elements in the CrFeCoNiPd NP were still uniformly distributed after oxidation, as shown by the EDS mapping in Fig. 1(b). Hence, more extensive oxidation occurred in the CrMnFeCoNi NP compared with the CrFeCoNiPd NP over the same reaction duration.

Our in situ high-resolution TEM (HRTEM) observations reveal the dynamic oxidation processes in CrMnFeCoNi and CrFeCoNiPd NPs. Figures 2(a)-2(f) show the time-series HRTEM images of oxidation in a CrMnFeCoNi NP (see Movie ESM1). As the NP was exposed in an O₂ environment for approximately 10 min, nanoislands formed on its surface covered with an ultra-thin oxide layer. In Figs. 2(a)-2(f), a nanoisland appeared as a half ellipsoid, indicative of a tendency to minimize its surface energy [29]. This nanoisland has the spinel structure of [112]-MnCr₂O₄ with the lattice constant of a = 8.61 Å (see Fig. S2 in the ESM). As the MnCr₂O₄ structure is metastable at low temperatures [30], its morphology further evolved due to destruction of the crystalline structure. Two small amorphous particles, as indicated by the white arrows in Fig. 2(c), first nucleated and grew on the surface of the MnCr₂O₄ nanoisland, then moved toward each other, and finally coalesced into a new nanoisland with lattice fringes, as shown in Fig. 2(f). At this stage of oxidation, other MnCr₂O₄ nanoislands frequently emerged, for example, at the site indicated by the brown arrows in Fig. 2(d). We note that Fe atoms were likely involved in the formation of surface oxides, as indicated by the EDS mapping results in Fig.1. However, it is hard to determine the crystal structure of Fe-containing oxides because they exhibit one-dimensional (1D) lattice fringes distributed in small regions. In addition, the curved



Figure 1 Comparison of the CrMnFeCoNi and CrFeCoNiPd NPs after *in situ* oxidation experiment. HAADF image of an oxidized CrMnFeCoNi NP (a) and an oxidized CrFeCoNiPd NP (b), together with EDS mapping of all the elements involved. Scale bar, 20 nm.



Figure 2 A series of HRTEM images showing the *in situ* oxidation process of a CrMnFeCoNi particle at \sim 50 °C. The nanoislands of MnCr₂O₄ underwent dynamic destruction in (a) and (b) and reconstruction in (c)–(f). Another typical MnCr₂O₄ nanoisland was indicated by the brown arrow in (d). Scale bar, 5 nm.

metal-oxide interface (traced by the white dotted line in Fig. 2) indicated non-uniform oxide growth at different positions, which also resulted in local stripes of lattice fringe as indicated by the yellow arrow in Fig. 2(c). Since no dislocation structure or other type of structural defect was observed nearby, these stripes were likely caused by lattice strains from local reactions [31]. The oxidation reaction entered a state of dynamic equilibrium, and the thickness of the oxide layer remained nearly unchanged after 40 min oxidation. The thickness of the oxide layer as measured increased by about 41% (from 6.66 to 9.42 nm). Movie ESM1 shows *in situ* observations of the above oxidation process.

To compare with the dynamic oxidation process in CrMnFeCoNi NPs, we performed in situ oxidation experiments of CrFeCoNiPd NPs, which replaced Mn with the noble metal element Pd while keeping the other four alloying elements unchanged. Figures 3(a) and 3(b) show the HRTEM images taken in sequence at two different locations during the oxidation process of a CrFeCoNiPd NP. Numerous nanolamellas containing clearly visible atomic layers (marked by the blue arrows in Fig. 3(a)) nucleated and grew at the surface of the preexisting oxide layer. Notably, the distances of lattice spacing (d-spacing) of the nanolamellas were measured as 2.77 and 2.80 Å, larger than the largest d-spacing in the face-centered cubic (FCC) HEA NPs (2.08 Å of {111} planes) [32]. These nanolamellas were identified as [110]-CrO₂ with the rutile structure, by comparing its fast fourier transform (FFT) pattern (inserted in Fig. 3(a)(3)) with the standard diffraction patterns of various oxides (see Fig. S3 in the ESM). The CrO₂ nanolamellas grew layer by layer on their surface (see Movie ESM2), indicative of outward diffusion of Cr through the CrO₂ oxide. The observed formation of CrO₂ nanolamellas on the surface of the CrFeCoNiPd NP is consistent with previous studies which demonstrated that Cr usually has a high diffusion rate during the oxidation process, thus forming an oxide scale containing Cr on the surface of bulk HEAs [13, 18]. In concurrence with the surface growth of CrO₂ nanolamellas, another crystalline phase appeared at the metal-oxide interface, as indicated by purple arrows in Fig. 3(a). This interfacial phase presented a typical [110]-FCC diffraction pattern with the d-spacing of 2.48 Å of {111} planes, which is close to that of FeO{111} (2.42 Å) and NiO{111} (2.50 Å). Since Ni was not obviously present in the oxide layer (as shown in the EDS mapping in Fig. 1(b)), we infer that the interfacial phase was FeO, which is also in agreement with the relatively low diffusion rate of Fe in previous studies [13]. The oxidation process at another region of the same particle is shown in Fig. 3(b). Similarly, we observed the formation of [001]-CrO2 (indicated by the blue arrows) on the NP surface and the formation of [001]-FeO (indicated by the purple arrows) at the metal oxide interface. Unlike the layer-by-layer formation of surface CrO2, FeO nanocrystals suddenly appeared; before their appearance, only strong fluctuations of image contrast were observed in the same area. The evolution of FeO nanograins was recorded in Movie ESM3. We note that the fast formation of FeO nanograins was accompanied with a significant change in the position of the local metal oxide interface (as marked by the red dashed lines in Fig. 3). This indicates that the Fe atoms may have diffused outward from the metal matrix and then reacted with the oxygen diffusing inward at the metal oxide interface. Although the EDS mapping of



Figure 3 HRTEM image sequences of the dynamic oxidation process at two different regions (shown in (a) and (b)) in a CrFeCoNiPd NP at ~ 50 °C. The insets show the FFT patterns of newly formed FeO and CrO₂. Scale bar, 5 nm.

the CrFeCoNiPd NPs after oxidation also detected Co in the oxide layer (as shown in Fig. 1(b)), the Co-containing oxide was not found. In general, the formation of CrO_2 and FeO nanocrystals contributes substantially to the increase of crystallinity of the oxide layer. After the above observations, the oxidation rate of the CrFeCoNiPd NP slowed down. The thickness of the oxide layer increased by about 19% (from 8.23 to 9.78 nm) after 40 min of *in situ* oxidation. Note that the *in situ* oxidation product of Cr was CrO_2 , which contrasts with Cr_2O_3 normally observed after oxidation of bulk materials at elevated temperatures [33]. This can be ascribed to different temperatures as well as different time and length scales involved in the oxidation processes. Future studies are needed to gain an in-depth understanding of the impact of these differences.

To compare the oxidation response of HEA NPs from *in situ* observations with those of their bulk counterparts, chemical analysis was carried out on the surface oxides of the bulk samples of CrMnFeCoNi (Fig. 4(a)) and CrFeCoNiPd (Fig. 4(b)) after oxidation at room temperature (~ 35 °C). As shown in Fig. 4(a),

the broad distribution of O indicates that oxidation occurred all over the surface of the bulk CrMnFeCoNi HEA. The top half of a micro-sized particle on the sample surface in Fig. 4(a) is crystalline, while the lower half is amorphous. Figure 4(c) shows the HAADF-STEM image of the top part of this micro-particle and the corresponding element distribution maps, indicating the oxide structure of [100]-MnCr₂O₄. Furthermore, according to the quantitative EDS analysis extracted from the maps, the atomic ratio of Mn:Cr:O in this region was close to 1:2:4 (see Fig. S4 and Table S1 in the ESM). Hence, the favored oxidation product of the bulk CrMnFeCoNi HEA was MnCr2O4, consistent with our in situ results of CrMnFeCoNi NPs. However, for the bulk CrFeCoNiPd HEA (Fig. 4(b)), the majority of O was observed in small particles where the concentration of Cr was also high, indicating the selective oxidation of Cr. A detailed chemical analysis suggests that Cr was likely oxidized to a mixture of Cr₂O₃ and CrO₂ (see Fig. S5 and Table S2 in the ESM). Compared to CrO₂, Cr₂O₃ is considered as a more stable oxide, which is a common oxidation product of HEA alloys containing Cr [33, 34].



Figure 4 Chemical characterization of bulk HEAs. (a) and (b) HAADF images of CrMnFeCoNi and CrFeCoNiPd HEAs with corresponding EDS maps after oxidation at room temperature (~ 35 °C). (c) High resolution HAADF-STEM image of the top part of a micro-sized particle on the surface of the CrMnFeCoNi HEA in (a) and the corresponding elemental distribution maps. Scale bar, (a) and (b): 1 µm, (c): 1 nm.

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The above experimental results have revealed the effects of different elements on the oxidation process in HEAs. We observed highly dynamic processes of oxidation, resulting in non-equilibrium oxide phases and structures. It is not yet feasible to resolve all the oxidation products and element distributions. Nonetheless, our in situ observations reveal the distinct oxidation responses of CrMnFeCoNi and CrFeCoNiPd NPs. In the CrMnFeCoNi NP, a favorable oxide product is MnCr₂O₄ with the spinel structure, which indicates that Mn and Cr are more reactive with O than the other three elements. In the CrFeCoNiPd NP, the reactive element Mn is replaced by the inert element Pd. As a result, a favorable oxide product is CrO₂ with the rutile structure, which indicates that Cr is more reactive with O than the other four elements. CrO₂ forms on the NP surface and thus is a result of Cr outward diffusion through the oxide layer. In addition, FeO nanocrystals form at the oxide/metal interface and they are a result of O inward diffusion through the oxide layer.

To further understand the oxidation of HEAs beyond the classical theory of metal oxidation [35], we performed first principles studies of oxide formation energies and diffusion rates in the HEAs of CrFeCoNiPd and CrMnFeCoNi through DFT calculations and AIMD simulations. The lattice constants of the two HEAs with FCC structure have been determined by DFT calculations, giving the value of 3.67 Å for CrFeCoNiPd and 3.54 Å for CrMnFeCoNi. This suggests a 3.36% increase of the lattice constant by replacing Mn atoms in CrMnFeCoNi with larger Pd atoms in CrFeCoNiPd. In addition, the energies of three oxides, CrO2, FeO, and MnCr2O4, were evaluated with DFT calculations. Their crystal structures were set up based on TEM results. We considered the general oxidation reaction, $M + (x/2)O_2$ \rightarrow MO_x, and calculated the formation energy on a per-O₂molecule basis. Table 1 lists the calculated formation enthalpy (per O₂ during oxidation), atomic volume, magnetic moment, and space group for CrO₂, FeO, and MnCr₂O₄. Among these three oxides, MnCr₂O₄ gives the lowest formation enthalpy, suggesting its favorable energetics of oxidation compared to CrO2 and FeO. These calculations are consistent with our observations in Figs. 2 and 3.

Table 1 Formation enthalpy, atomic volume and magnetic moment for threeoxides, CrO_2 , FeO, $MnCr_2O_4$ as from DFT calculations

Oxide	Formation enthalpy (eV, per O ₂)	Atomic volume (ų)	Magnetic moment (μB, per atom)	Space group
CrO ₂	-6.131	10.042	0.667	P4 ₂ /mnm
FeO	-5.051	10.078	2.0	Fm3m
$MnCr_2O_4$	-8.124	11.323	0.429	$Fd\bar{3}m$

Moreover, diffusion of vacancies in both CrFeCoNiPd and CrMnFeCoNi was studied by AIMD simulations [22, 23]. The vacancy diffusion coefficients, D^* , of each type of element, were calculated from $D^* = (\langle r^2(t) \rangle)/6t$, where $\langle r^2(t) \rangle$ is the mean squared displacement (MSD), based on the atomic trajectories from AIMD simulations [36], and they are given in Fig. 5. In the CrMnFeCoNi HEA, Mn and Cr atoms were involved in the formation of MnCr₂O₄, which would require high diffusion rates of the two elements in the alloy matrix, as supported by high values of D^* in Fig. 5. In the CrFeCoNiPd HEA, the value of D^* for Pd atoms is high, despite the large size of Pd atoms. However, Pd is inert to oxidation and thus moves by fast random diffusion, leading to a homogeneous distribution of Pd in the core of the CrFeCoNiPd NP under surface oxidation, as shown in Fig. 1. This result implies that larger atoms can move faster than smaller atoms for vacancy diffusion, which is consistent with a previous



Figure 5 AIMD simulation results of vacancy diffusion. Diffusion coefficient of each type of atoms for vacancy diffusion in CoCrFeNiMn and CoCrFeNiPd HEAs at 1,500 K from AIMD simulations; four independent configurations were analyzed for each HEA.

study that rationalized this trend based on bonding characteristics of the d electrons of alloying atoms [37]. Although Pd exhibited the largest diffusion rate, it was less prone to oxidation in the CrFeCoNiPd (Fig. 3). In addition, Mn and Cr in CrMnFeCoNi have higher D^* values than Cr in CrFeCoNiPd. This result is in line with faster formation of MnCr₂O₄ in CrMnFeCoNi NPs than CrO₂ in CrFeCoNiPd NPs. Nevertheless, the oxidation resistance of HEAs can be influenced by a number of factors related to the chemical potentials and diffusion coefficients of constituent alloying elements and warrant further systematic studies in the future.

4 Conclusions

We have conducted in situ E-TEM observations of oxidation in CrMnFeCoNi and CrFeCoNiPd NPs near room temperature. The oxidation processes and products of the two HEA NPs are drastically different because the reactive element Mn is replaced by the inert element Pd. However, Cr remains a highly reactive element in both types of HEAs, yielding the spinel MnCr2O4 for CrMnFeCoNi NPs as opposed to the rutile CrO₂ for CrFeCoNiPd NPs. Similar oxide products are also observed on the surface of the corresponding bulk HEAs. We also performed oxidation experiments of FeCoNiCr NPs to further demonstrate the influences of Pd vs. Mn on oxidation behavior of HEA NPs (see the ESM for details). These results suggest that the oxidation resistance of complex multi-principal element alloys can be changed significantly by only replacing one constituent element. In HEA NPs, metastable oxides often form, because the non-equilibrium processes of oxidation can be strongly influenced by small particle size and large surface area. Our work provides a glimpse into the intriguing oxidation responses of HEA NPs and may motivate further in-depth studies to understand and control the oxidation of HEAs at the nanoscale.

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Electronic Supplementary Material: Supplementary material (*in situ* oxidation observations of oxidation of a CrMnFeCoNi HEA NP at ~ 50 °C (Movie ESM1); *in situ* observation of oxidation of a

CoCrFeNiPd HEA NP at ~ 50 °C. (Movie ESM2); in situ observation of another region of the same CoCrFeNiPd HEA NP (Movie ESM3); initial morphology of NPs before in situ oxidation test; the detailed characterization of oxides (Figs. S1-S5, Tables S1 and S2)) is available in the online version of this article at https://doi.org/10.1007/s12274-021-3900-3.

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