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Oxidation study of CoCrCuFeNiSix high entropy alloys

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**Abstract**

Oxidation studies of Co–Cr–Cu–Fe–Ni–SiX(0,0,3,0.6,0.9) high entropy alloys (HEA) at 600, 700 and 800 °C for 30 h are performed in the present work. Isothermal oxidation confirmed that the oxidation resistance of Co–Cr–Cu–Fe–Ni–SiX(0,0,3,0.6,0.9) high entropy alloy increases with Silicon (Si) content up to 0.6%, beyond that it decreases. Oxidation rate kinetics study of all the alloys at the three designated test temperature represented the typical cubic curve. X-ray diffraction (XRD) analysis revealed the evolution of Cu oxide (CuO) along with existing phases in all the HEA samples. Microstructural observation after oxidation test exhibited an increase in oxide formation with the oxidation temperature. To comprehend the kinetics of oxidation more clearly, Arrhenius plots were drawn for all the HEA samples and activation energies are calculated.

**1. Introduction**

In recent years, novel alloys that contain multi-elements have been developed to improve the chemical, physical and mechanical properties. In contrast to conventional alloys, High entropy alloys (HEA) constitutes five or more principal elements in which the concentration of each has an almost equimolar ratio. It was distinguished that HEA composes of the simple solid solution rather than forming intermetallic compounds or complex phases due to sluggish diffusion and high mixing entropies, which further abates the brittleness of the material [1, 2]. Relying on the compositional and structural features possessed by HEA, it leads to high thermal stability, oxidation and superior mechanical properties such as tensile strength, fatigue strength, etc [3–6]. HEA grabs attention in different research areas which are currently in progress as they exhibit exceptional properties that are credible to engage in various applications [7, 8] at both ends of temperature (low and high temperatures) [9–11].

Fundamentally, HEA demonstrates four possible core effects: (1) High entropy effect [12] which attributes in the improvement in high-temperature (thermal) stability. (2) Kinetics of phase transformation in HEA become slower compared to conventional alloys due to retaining sluggish diffusion [13]. (3) HEA shows awful lattice distortion, which is known to hinder the free movement of dislocations and thus lowers the electrical and thermal conductivity [14]. (4) Due to attributing cocktail effect, HEA shows remarkable properties over the consolidated superior properties of individual elements [15, 16]. It was presumed that one or more of these four core effects perform a vital role in altering the physical and chemical properties of HEA.

There are some reports on HEAs showing excellent oxidation resistance and till date, oxidation resistance has been investigated on selected types of high entropy alloys viz., Cu–Cr–Co–Fe–Ni, Al–Cr–Fe–Ni–Co–Cu, and Cr–Mn–Fe–Co–Ni, etc. Kim et al [17] have studied the oxidation behavior of Cr–Mn–Fe-Co–Ni high entropy alloy in which, both Cr and Mn evidences significant effect on the oxidation behavior of HEA. The study on Co–Cr–Fe–Ni–Al(x = 0.15, 0.4) HEA system in supercritical water in comparison with HR3C steel reported that Co–Cr–Fe–Ni–Al, HEA system shows better oxidation resistance than HR3C steel and the properties of HEA are greatly affected by Al addition [18]. Similarly, Liu et al [19] and Kumar et al [20] also reported on Co–Cr–Fe–Ni–Al0.3–Si and Al–Co–Cr–Cu–Fe–Ni–Si HEA systems, respectively, where they observed that inclusion of Si promotes BCC phase evolution than FCC. Among all the HEAs,
Co–Cr–Cu–Fe–Ni–Si, based alloy is one of the vital alloys which exhibits the most superior properties such as wear resistance, microhardness, oxidation resistance, etc. Recently, in our previous work, [21] Co–Cr–Cu–Fe–Ni–Si, HEAs were synthesized via vacuum arc melting and spark plasma sintering, and the study reported that increase in Si content leads to better microhardness and wear resistance for both the cases those are processed differently. Also, Co–Cr–Cu–Fe–Ni–Si, HEA prepared by spark plasma sintering process provided superior physical properties compared to the vacuum arc melting process due to the existence of sigma phases. However, the effect Si on the oxidation behavior of HEAs was not yet elucidated. Hence, the current work focuses on the detailed effect of Si content on the oxidation behavior of Co–Cr–Cu–Fe–Ni–Si, HEA at different oxidation temperatures viz., 600 °C, 700 °C, and 800 °C and to study the phase formation and microstructural changes after oxidation test.

2. Experimental procedure

The high entropy alloy employed in this study was Co–Cr–Cu–Fe–Ni–Si\(_{X=0-0.3; 0.6; 0.9}\). Four different HEA samples were synthesized differing in Si content. HEA without Si content (0% Si) designated as HEA-1, 0.3% Si, 0.6% Si, 0.9% Si were assigned to HEA-2, HEA-3 and HEA-4, respectively. Initially, elemental powders were processed by a high energy ball mill for 10 min to prepare a blended mixture of Co, Cr, Cu, Fe, Ni, and Si powders. The mixed and blended powder was consolidated in a graphite die of 10 mm diameter followed by processed differently. Also, Co–Cr–Cu–Fe–Ni–Si, HEA prepared by spark plasma sintering (SPS) at 1000°C for 5 min under uniform pressure of 60 MPa. In the heat treatment cycle, the initial heating rate was maintained at 100 °C min\(^{-1}\) from 570 °C to 800 °C. Later it was decreased to 50 °C min\(^{-1}\) until the temperature reached 1000 °C [21]. Isothermal oxidation temperatures were chosen in the range of 06–08 T\(_m\), of the lowest melting element (Cu) of the alloys.

The density of the sintered samples has been measured by Archimedes’ principle, weighing them both in air and water using an electronic balance having a precision of 0.1 mg. The obtained samples were freshly ground by belt grinder before the oxidation tests. Muffle furnace was utilized to perform isothermal oxidation test at different temperatures viz., 600, 700, 800 °C for 30 h under the presence of excess air. The initial weight of each sample was noted before the oxidation test. Similarly, after every 5 h of 30 h test, the sample’s weight was measured precisely.

Phase identification and microstructural analysis of the samples were carried out by x-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Characterization was done before and after the oxidation test for comparison. Bruker D8 Advanced x-ray diffractometer fitted with Cobalt K alpha (\(\lambda = 1.79 \, \text{Å}\)) target was used for XRD analysis. JEOL JSM-6084LV was employed for SEM study. From the cumulated weight gain plot, rate kinetics of the oxidation process was analyzed and finally, the activation energy of the process was measured for each HEA.

3. Results and discussion

3.1. Microstructural analysis

Figures 1(a)–(l) shows the SEM micrographs of all HEA samples after the isothermal oxidation tests for 30 h at various temperatures (600, 700 and 800 °C). Figures 1(a)–(c) represents HEA-1 sample (Co–Cr–Cu–Fe–Ni–Si \(_{X=0}\)) after the oxidation test at 600, 700 and 800 °C respectively. HEA-1 sample i.e., HEA without Si addition shows the evolution of phases with different morphologies with respect to the temperatures. At a higher temperature of oxidations, a coarse structure was observed, which might be due to higher growth rate kinetics of the oxidation process was analyzed and finally, the activation energy of the process was measured for each HEA.

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The SEM micrographs of HEA-2 (Co–Cr–Cu–Fe–Ni–Si \(_{X=0.3}\%\)) and HEA-3 (Co–Cr–Cu–Fe–Ni–Si \(_{X=0.6}\%\)) are illustrated in figures 1(d)–(f) and figures 1(g)–(i), respectively. Addition of Si results into the morphological changes of oxide layer surface. The careful analysis of SEM images indicates the marginally fine or similar microstructure for a particular oxidation temperature. On the other hand, HEA-4 (Co–Cr–Cu–Fe–Ni–Si \(_{X=0.9}\%\)) indicates a different trend, as illustrated in figures 1(j)–(l). Comparative analysis of figures 1(i) and (l) clearly indicates that, when Si addition reaches to 0.9%, the coarser microstructure of the oxide layer became coarser. Moreover, the oxide layer in figure 1(l) appeared delaminated or less compact in nature, which can easily allow more air ingestion during oxidation.

The formation of the strong oxide layer can be attributed to the coarser microstructure at a higher temperature and the same reasoning leads to the fact that 0.9% Si added HEA (HEA-4) shows more oxidation than 0.6% Si HEA (HEA-3). Thus, it can be concluded that oxide formation on the sample surface decreased with increasing Si content in the alloy up to 0.6% and the effect of Si content on oxide formation diminished above 0.6% Si.
3.2. XRD analysis

XRD analysis of the as-synthesized and oxidized HEA samples was presented in figure 2. It is observed that as-synthesized samples (marked as room temperature in the figure) showed two FCC peaks and σ phase peaks. As, Cu has high positive mixing enthalpy with other constituent elements in the alloy, thus, Cu tends to segregate at the grain boundaries which led the formation of F2 phase. Whereas, the F1 phase could be the Ni–Fe–Co FCC phase with some amount of Cr and Cu as Ni is an FCC austenite stabilizer in Ni-containing steels \[21\]. After oxidation, the formation of CuO along with existing FCC solid solutions and σ phase was observed in all the HEA samples. In spite of the presence of different elements, only Cu was oxidized due to its lower oxidation resistance in the present temperature range of discussion \[22–25\]. During high-temperature oxidation, ionic diffusion plays a major role by transferring metallic cation and oxygen anion. Apart from this, any defect in the structure like pores, cracks, etc may also play a role. During the oxidation process, CuO oxide forms first as Cu is less stable just above 300 °C \[26–30\]. After that, the remaining elements start oxidizing oxidized. i.e. Cr > 400 °C \[31, 32\], Ni > 500 °C \[31, 32\], Fe > 700 °C \[33, 34\], Co > 700 °C \[35, 36\] and Si > 700 °C \[37–44\]. However, FeO, CoO and SiO₂ will be perfectly stable above 900 °C \[33–44\]. Due to this reason, primarily Cu oxidizes in the present study as per detection by XRD.

In any of the HEAs shown in figure 2, it was observed that relative intensities of CuO peaks increase with the increase in oxidation temperature. It may be due to an increase in the oxide layer thickness. So, CuO intensity was more at a higher temperature in comparison to the original FCC and σ phases. This observation is similar in

![Figure 1](image_url).
each of the plots of figures 2(a)–(d). From this trend, it can be concluded that the higher temperature of oxidation leads to more oxidation products.

When XRD profiles of all HEAs are compared at a particular temperature, it can be seen that the relative intensities of the CuO peak are similar in HEA-1 and HEA-2 and it decreases remarkably in HEA-3. Further, the relative intensity of CuO XRD peak increased when Si addition was 0.9% (HEA-4). From this observation, it can be reported that with the increase in Si content from 0 to 0.6% the CuO formation shown diminishing trend due to a lesser extent of oxidation. However, the addition of Si in HEA beyond 0.6% lead to higher oxidation or, it can be concluded that HEA-4 possess lower oxidation resistance compared to HEA-3.

3.3. Oxidation kinetics of HEAs

Figures 3(a)–(c) shows the isothermal oxidation test plots (actual values and best fits) of HEAs with altering Si content at different temperatures (600, 700 and 800 °C) for a period of 30 h. Weight gain values were measured after every 5 h time interval during the oxidation test.

During the study of the weight gain trend (actual points on the plots), following observations were made: for Si-containing HEAs, there was no substantial weight difference with increase in the oxidation time period from 0 to 5 h at 600 °C, above which weight gain was observed at every 5 h interval till 30 h in all samples. However, Si-containing samples showed lower weight gain than HEA-1. A similar trend was also observed at 700 and 800 °C oxidation temperature. By comparing mass gain values at a particular time interval, it was observed that the Si-containing HEA samples showed higher oxidation resistance than HEA-1 at all oxidation temperatures considered in this study.

When the trend was studied with variation in Si amount, it was noticed that 0.3% Si (HEA-2) shows lower weight gain than HEA-1. Similarly, HEA-3 (0.6% Si) shows a lower gain in weight than HEA-2. But, HEA-4 (0.9% Si) shows higher weight gain than HEA-2 and HEA-3. But, HEA-4 shows lower weight gain than HEA without Si addition (HEA-1). Thus, the sample with 0.9% Si content (HEA-4) experienced lower oxidation than the 0% Si sample (HEA-1) and greater oxidation than the remaining samples (HEA-2 and 3) which confirms the microstructural results of oxide formation. Further, it is worth to mention here that XRD peak intensities of CuO described the same tendency (figure 2).

The decrease in oxidation after the addition of Si (up to 6%) can be explained by the following: 1) During spark plasma sintering process F1, F2 and σ phases were formed, out of which F2 phase contains maximum Cu [21]. Therefore, F2 is preferentially oxidizing as CuO was the only oxide peak in figure 2. Additionally, with increasing Si content, the amount of F2 phase fraction decreases, as discussed in our previous work [21]. Hence,
the decrease in the phase fraction of oxidation prone phase (F2) leads to lesser oxidation. Amongst the constituent elements of the HEAs, Cu having the lowest melting point is most oxidation prone. On the other side, \( \sigma \) is an oxidation-resistant phase as it mainly contains Co, Cr, Fe and Ni, along with added Si\[21, 45–48\]. The amount of sigma phase increases with Si addition resulting in more oxidation resistance alloy. (2) The addition of Si leads to a decrease in the lattice parameter \[21\] and hence introduces lattice distortion. Lowering of lattice parameter leads to lesser bulk diffusion of oxygen or cations, which in turn decreases oxidation. The aforementioned discussion is valid up to 0.6% Si (HEA-3) while HEA-4 showed higher oxidation. This can be explained by the following:

(1) After SPS, different samples contained different amounts of porosity, as observed from porosity measurement results of as-sintered HEAs. HEA-1 showed 99.2% theoretical density, HEA-2 98.5%, HEA-3 97.8%, and HEA-4 97.0% only. With the addition of Si, more sigma phase formation was observed, resulting in more strength of the synthesized HEAs \[21\], but at the same time, defects like porosity increase marginally. A similar observation was also noticed during laser-Ignited Self-Propagating Sintering of AlCrFeNiSi HEA and on another as-cast multicomponent system \[49, 50\]. In the present system, this could happen due to non-accommodated thermal stress generated during cooling after the SPS process. The presence of more amount of hard/brittle compound phase (sigma) at higher Si content leads to higher porosity during the cooling process itself. Moreover, as the lattice parameters of all the constituent phases decrease with higher Si content \[21\], the shrinkage may lead to porosity during the synthesis. The effect of such a marginal change of porosity on mechanical strength was not visible. But, the same plays a role in oxidation as it helps in oxygen ingestion apart from slow anionic diffusion of oxygen. This phenomenon provides an opposing effect of Si added oxidation improvement leading to a breakeven value at 0.6% Si. So, at 0.9% (HEA-4), porosity plays a more detrimental effect than the oxidation resistance effect of Si as discussed in the last paragraph. The presence of a minor amount of pores is also visible from the SEM image of SPS alloys (figure 3, \[21\]). From the images, it was observed that, with increasing Si content in the alloy, the percentage of porosity was increased. Small pores were settled down on the grain boundaries (mainly at the triple point) in the case of HEA-1, 2, and 3. However, with further increase in Si content beyond the 0.6 percentages, pores are visible both inside grain along with grain boundaries. This mechanism can lead to higher oxidation \[51\].

![Figure 3. Isothermal oxidation plot (mass gain versus time) of HEA (Co–Cr–Cu–Fe–Ni–Si \( _{X=0,0.3,0.6,0.9} \)) samples oxidized at (a) 600 °C, (b) 700 °C, and (c) 800 °C.](image-url)
As Si addition leads to lattice distortion and formation of the hard sigma phase, at 0.9% Si, the HEA becomes too brittle during high-temperature oxidation study leading to a porous oxide layer (figure 1(l)). This can lead to further oxidation of the underneath layer.

To understand the oxidation rate kinetics, the weight gain values of figure 3 were tried to be fitted with various oxidation models. Earlier, it was reported that the oxidation kinetics of Cr–Mn–Fe–Co–Ni HEA obey parabolic law at operating temperatures above 900 °C [15]. Several trials have been made to fit the present values with the following parabolic equation with parabolic rate constant $k_p$ [15]

$$\Delta m^2 = k_p t + c_0$$

where, $\Delta m$ and $t$ represent mass gain and the oxidation time, respectively, $k_p$ and $c_0$ are constants. After the parabolic fitting of all oxidized samples’ plot at different temperatures, it was noticed that the fits were inconsistent and coefficient of determination ($R^2$) values were low.

In another oxidation study of electrodeposited reduced graphene oxide (RGO) reinforced copper coating, it was reported that above the 400 °C the Cu rich matrix follows the cubic rate law [22]:

$$\Delta m^3 = k_c t + c_0$$

where, $\Delta m$ and $t$ represent mass gain and the oxidation time, respectively, $k_c$ and $c_0$ are constants. When the cubic fit was examined on the present data (all temperatures), satisfactory $R^2$ values were obtained. The obtained $R^2$ values are illustrated in table 1 and the corresponding fits are shown in figure 3 with continuous lines (without data points). From these fitted plots, rate constants were calculated as per the above equation at different isothermal oxidation temperatures (600, 700 and 800 °C) and listed in table 1.

Additionally, data fitting was also tried with another common oxidation model, i.e., logarithmic, but the coefficient of determination value was low.

To comprehend the kinetics of oxidation, the Arrhenius plots of $\ln(k_c)$ versus $1/T$ were drawn for all the HEA samples as displayed in figure 4. Activation energies of the oxidation process were calculated from the straight-line fit and Arrhenius equation. Obtained values are indicated in table 1. Amongst all, the HEA-1 sample has got the lowest activation energy, which means it has a high tendency of oxidation at this temperature range. Lower activation energy signifies ease of oxygen diffusion on the sample surface and the sample becomes more oxidized at higher temperatures as the exposure time increases. Nevertheless, the HEA-4 of having 0.9% Si content exhibits lower oxidation resistance than that of the remaining two samples (HEA-2 and 3). The same trend was observed and explained in figure 3. However, this is worth mentioning that the activation energy values measured here are not indeed their materials property, as they were affected by structural defects like porosity.

4. Conclusions

The high-temperature oxidation behavior of Co–Cr–Cu–Fe–Ni–Si$_x$($x=0.0, 0.3, 1, 3.0, 6.0$ and $9.0$%) HEA samples at 600, 700 and 800 °C for 30 h was investigated and the following conclusions can be drawn.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Sample & Temperature (°C) & Fitted $R^2$ value (%) & Rate constant ($k_c$) & Activation energy (kJ mol$^{-1}$) \\
\hline
HEA-1 & 600 & 96.782 & 0.500 & 4.194 \\
 & 700 & 99.953 & 0.625 & \\
 & 800 & 98.936 & 0.650 & \\
HEA-2 & 600 & 95.463 & 0.406 & 9.315 \\
 & 700 & 98.947 & 0.686 & \\
 & 800 & 99.358 & 0.710 & \\
HEA-3 & 600 & 97.813 & 0.232 & 14.484 \\
 & 700 & 98.720 & 0.458 & \\
 & 800 & 99.860 & 0.595 & \\
HEA-4 & 600 & 99.492 & 0.517 & 7.045 \\
 & 700 & 98.903 & 0.806 & \\
 & 800 & 99.053 & 0.900 & \\
\hline
\end{tabular}
\caption{Oxidation study parameters of HEA samples (Co–Cr–Cu–Fe–Ni–Si$_x$($x=0.0, 0.3, 1, 3.0, 6.0$ and $9.0$%)) after isothermal oxidation at different temperatures.}
\end{table}
1. The microstructure of all oxidized HEA samples demonstrated the formation of oxide layer on the surface. Among all the HEAs, the sample with 0.6% Si content shows the lowest oxide growth at all the three test temperatures and indicates the best oxidation resistance.

2. XRD analysis of all the HEAs revealed the CuO along with other peaks as the effect of oxidation.

3. Oxidation kinetics of all the HEAs displays cubic law in weight gain trend.

4. The highest activation energy was achieved in HEA sample with 0.6% Si content, which yields enhanced oxidation resistance compared to the other HEAs taken under consideration. Decrement of F2 phase attribute to the higher activation energy. However, porosity and brittle oxide layer led to a decrease in activation energy after the addition of 0.9% Si.

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