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High temperature oxidation of non equi-atomic Al$_{5}$Cr$_{12}$Fe$_{35}$Mn$_{28}$Ni$_{20}$ high entropy alloy

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Abstract

The Oxidation behavior of the Al$_{5}$Cr$_{12}$Fe$_{35}$Mn$_{28}$Ni$_{20}$ high entropy alloy was investigated in air at temperatures 900 °C, 1000 °C and 1100 °C for 100 h isothermally. The oxidation kinetics at all temperatures obeys the parabolic rate law with an activation energy 100.6 kJ mol$^{-1}$. The alloy was externally oxidized forming duplex layer consisted of manganese oxides that overlays Mn-Cr-Fe spinel oxides. While, it was observed that at 1000 °C and 1100 °C the samples were also oxidized internally forming Al$_2$O$_3$ deep in the alloy. The internal oxidation behavior of the alloy oxidized at 1000 °C for 1 and 24 h producing external scale of Mn$_3$O$_4$ overlaying Mn-Cr-Fe spinel oxide and Al$_2$O$_3$ precipitates.

1. Introduction

High entropy alloys are new class that emerged precisely two and half decades ago. Unlike the conventional alloys, this alloy lack the presence of single principle element and is a multi-component system that consists primarily of five or more metallic elements in equi-atomic or nearly equi-atomic proportions ranging from 5–35 at. %. HEAs can contain concentrations of minor elements each below 5 at. % to modify and tailor specific properties [1]. Besides as its name indicates, this alloy displays ideal high configurational entropy of mixing which equals to 1.5 R and favors the formation of solid solutions giving simple microstructures without complexities [2]. This simplicity of microstructure enhances the existence of unique combination of properties such as high strength, high hardness, good ductility, creep strength, corrosion, wear and oxidation resistance [3–11]. The solid solution formed in high entropy alloys are normally of Face-centered cube, Body-centered cube and Hexagonal-close packed [12–14].

High entropy alloys show a group of unique properties that could possibly compete and may overcome other conventional alloys mostly due to the main four core effects; High entropy effect for thermodynamics that involves determination of equilibrium state and microstructure, Sluggish diffusion which affects the diffusion and phase transformation kinetics, Severe lattice distortion, and Cocktail effect that directly affects the HEAs properties [15–19].

Although high entropy alloys fit as good candidate to substitute the heat-resistant alloys in high temperature services [2], it has not been applied yet in this application sector. However, they are limited industrially to usage in hard facing applications and as binders for hard metals [20]. Generally, this limitation is due to the lack of knowledge of their high temperature oxidation mechanisms and behaviors. The majority of studies are subjected on understanding the concept of formation, parameters that govern the solid solution formation, setting thermodynamics models for high entropy alloys and their enhanced chemical and mechanical properties. In general, the few investigations on oxidation behaviors of HEAs either provided microstructural or kinetic knowledge on the scale formed without giving the full insights.

The Al$_{5}$Cr$_{12}$Fe$_{35}$Mn$_{28}$Ni$_{20}$ HEA has shown the ease of fabrication through arc melting process and deformation up to 90% reduction in thickness. The fabricated HEA formed a single solid solution with FCC crystal structure and possessed good mechanical properties such as high hardness values [21, 22].
combination made it obligatory for more and further studies; such as investigating the oxidation behavior and examining the oxide phases of the alloy.

This article presents the oxidation behavior of the Al\textsubscript{5}Cr\textsubscript{12}Fe\textsubscript{35}Mn\textsubscript{28}Ni\textsubscript{20} HEA at different range of temperatures 900 °C-1100 °C in air through investigating its kinetics and the produced scale morphology.

2. Experimental procedures

2.1. Alloy Characterization

The Al\textsubscript{5}Cr\textsubscript{12}Fe\textsubscript{35}Mn\textsubscript{28}Ni\textsubscript{20} HEA was fabricated in arc melting furnace, re-melted twice to ensure homogeneity then cold rolled to thickness reduction of 90\% \cite{21, 22}. The samples were provided as thin sheets with dimensions 20*10*0.5 mm.

The elemental analysis was detected to ensure the chemical composition of alloy through X-ray fluorescence analyzer (Niton\textsuperscript{TM} XL3t GOLDD\textsuperscript{+}). The alloy was analyzed at different spots to obtain the constituents concentrations and to ensure the purity and homogeneity of the alloy as shown in table 1.

The density of the alloy was measured through Archimedes method, where $W_a = 1.02955$ g and $W_w = 0.89091$ and according to equation (1) \cite{23}:

$$\rho_{tr} = \frac{W_a}{(W_a - W_w)} \quad (1)$$

The theoretical density $\rho_{true}$ was calculated through equation (2) and shown in table 2.

$$\sum_{i=1}^{n} (\text{wt}\%_i \rho_{true}) \quad (2)$$

The sample characterization was previously investigated which showed formation of homogeneous single-phase solid solution with FCC crystal structure \cite{21, 22}. The microstructures showed a formation of a dendritic structure due to the rapid cooling process known as undercooling; the fine elongated dendritic structure is due to the severe deformation of rolling process that occurred.

2.2. Isothermal oxidation

The samples were cut by wire cutting machine into pieces with dimensions of 10.5*10*0.5 mm (±0.5). All faces were ground through silicon-carbide abrasive papers with grit size (600–1200) in order and then cleaned by alcohol.

The oxidation tests were carried out for continuous 100 h at three different temperatures 900 °C, 1000 °C and 1100 °C in dry air at a rate of 2 lit/min using the thermal gravimetric device with a vertical tube furnace, model EVA 12/300B–CARBOLITE GERO, and controller programmer 3216 P5. All the specimens were weighed before oxidation. The weight gain per unit area as a function of time was recorded during oxidation using the gravimetric method; where a microbalance with an accuracy of $10^{-4}$ g was used in this study. Two additional samples were oxidized for 1 h and 24 h at 1000 °C.

2.3. Oxide layer characterization

To identify the phases formed during oxidation, X’pert PRO PAN analytical diffractometer was used to obtain X-ray diffraction pattern using Cu Kα-radiation $\lambda = 0.15406$ nm, 40 kV and 30 mA. While the morphology of oxide surface was observed through Backscattered Scanning electron microscopy FEI inspect S50–Netherlands micrographs along with its chemical analysis via Energy dispersive X-ray spectroscopy Burker AXS–flash detector 410 M, Germany. The cross sections of oxidized samples were mounted in electrically conductive

| Table 1. The elemental analysis of AlCrFeMnNi |
|-----------------|-----|-----|-----|-----|-----|-----|
| Element         | Al  | Cr  | Fe  | Mn  | Ni  | Impurities |
| Wt%             | 2.45| 11.79|36.67|25.59|22.98|0.523       |

| Table 2. The alloy’s calculated and theoretical densities |
|-----------------|-----------------|-----------------|
| Calculated density $\rho_{tr}$, g cm\textsuperscript{-3} | Theoretical density $\rho_{true}$, g cm\textsuperscript{-3} | Densification % |
|-----------------|-----------------|-----------------|
| 7.4260675       | 7.7692612       | 95.58          |
Bakelite and prepared as previously mentioned for thickness observations and elemental distribution detection across the oxide scale using Backscattered SEM images, Line and Point EDAX analyses.

3. Results and discussion

3.1. Oxidation kinetics

The Continuously recorded mass gain over all surface area of investigated samples during isothermal 100 h of oxidation in flowing air at three different temperatures 900 °C, 1000 °C and 1100 °C are shown in figure 1. The weights of the specimens were recorded at interval times during the test and the weight gain was calculated. The oxidation behavior of the alloy seems to follow the parabolic rate law at all temperatures according to equation

$$\Delta W = k_p t^{1/2}$$

Where $\Delta W$ is the weight gain per unit area, $K_p$ is the parabolic rate constant and $t$ is the oxidation time. This equation yields a straight line when $t$ is plotted against $[\Delta W/A]^2$ as shown in figure 2. To quantify the oxidation kinetics, the parabolic rate constants $K_p$ of the $\text{Al}_5\text{Cr}_{12}\text{Fe}_{35}\text{Mn}_{28}\text{Ni}_{20}$ HEA obtained from the parabolic plot at 900 °C, 1000 °C and 1100 °C were $3.34 \times 10^{-11}$, $8.23 \times 10^{-11}$ and $1.42 \times 10^{-10}$ gm$^2$/cm$^4$.sec respectively.

When comparing the parabolic rate constant of the alloy with high temperature service alloy rates such as stainless steel alloys, and Ni- super based alloys which ranges between $(3.2 \times 10^{-11}$ to $4.9 \times 10^{-11})$,[26,27] it is found that the rate of $\text{Al}_5\text{Cr}_{12}\text{Fe}_{35}\text{Mn}_{28}\text{Ni}_{20}$ is slightly higher. This can be attributed due to the higher content of chromium in these alloys.

Figure 1. The variation of weight gain ($\Delta W/A$) against the oxidation time of $\text{Al}_5\text{Cr}_{12}\text{Fe}_{35}\text{Mn}_{28}\text{Ni}_{20}$ high entropy alloy at temperatures 900 °C, 1000 °C and 1100 °C in dry air for 100 h.

Figure 2. The variation of weight gain ($\Delta W/A$)$^2$ against the oxidation time of $\text{Al}_5\text{Cr}_{12}\text{Fe}_{35}\text{Mn}_{28}\text{Ni}_{20}$ at temperatures 900 °C, 1000 °C and 1100 °C in dry air for 100 h.
Assuming that the parabolic rate constants follow the Arrhenius equation (4), which indicates the amount of energy needed for the diffusional process.

\[ K_p = K_0e^{-\frac{Q}{RT}} \] (4)

Where, Q is the activation energy, R is the gas constant and T indicates the oxidation temperatures in kelvin. The activation energy, Q was estimated and calculated as 100.6 kJ / mol through the ln \( K_p \) versus \( 1/T \) (K \(^{-1}\)) as shown in figure 3. It should be mentioned that the determined activation energy value is an apparent value due to the formation of multiphase oxide scale.

3.2. Phase analysis of the Outer Oxide Layer

The crystallographic structure of alloy and the oxide scales at all temperatures were characterized through XRD patterns as shown in figure 4. The XRD pattern of alloy shows the formation of single FCC solution [21, 22]. While, the analyses of oxide patterns indicate the existence of three manganese oxides; Hausmannite (Mn₃O₄), and Manganese (III) oxide (Mn₂O₃), Manganese dioxide (MnO₂) out of the possible four oxides which can be thermodynamically formed according to Manganese-Oxygen phase diagram [28].

The crystallographic structure of scale formed on the samples oxidized for 1 and 24 h were investigated through the XRD patterns in figure 5 which showed the formation of; Hausmannite (Mn₃O₄) and spinel (MnCr₂O₄). The spinel oxide was been able to be detected; this could be due to the spallation of upper layer that was observed through SEM images.

3.3. Oxide scale morphology and cross section investigation

3.3.1. Oxide layer morphology of 100 h

The examination of micrographs of alloy in figure 6 indicate the presence of dendritic structure due to the rapid cooling process known as undercooling, the fine elongated dendritic structure is due to the severe deformation occurred [21, 22]. The elemental analysis conducted by EDAX on surface indicates the homogeneity and the absence of any secondary phases and thus re-assuring the formation of single-phase solid solution which agrees with the previous studies operated on the alloy [21, 22].
The oxide scale formed at the surface of samples through 900 °C, 1000 °C and 1100 °C for isothermal 100 h of oxidation were investigated through Backscattered SEM imaging along with their elemental analyses as shown in figure 7. The EDAX chemical analyses report the presence of Manganese, Oxygen, Chromium and iron. The cross-section SEM images and line-EDAX analyses of external oxides surfaces and substrate are shown in figure 8. At 900 °C the SEM and line EDAX indicate the formation of thick duplex oxide layers externally. The outer layer consisted of manganese oxides containing some chromium and iron while the sudden increase of chromium peak near the alloy-scale interface supports the formation of Mn-Cr-Fe spinel. The spinel phases were not detected by XRD analysis due to the thick manganese oxides layer that blocked the possibility of detection.

The cross-sections of specimens oxidized at 1000 °C and 1100 °C showed that the alloy was oxidized both externally and internally in figure 9. The line EDAX investigation presented that the alloy formed a duplex oxide layer similar to that formed at 900 °C; the outer layer consists of manganese oxides and the inner layer formed Mn-Cr-Fe spinel at the alloy-scale interface. While, the sudden increase of aluminum peaks beneath the surface supports the formation of inner aluminum oxide precipitates. It was found that the thickness of manganese oxides layer increases with increasing the temperature which could be explained as the outward diffusivity of manganese increases with the temperature. It was also observed the presence of depleted zone of manganese and increase of iron content beneath the metal-scale interface.
3.3.2. Oxide layer morphology after 1 and 24 h

The alloy was also oxidized at 1000 °C for 1 and 24 h at the same atmospheric air conditions. This is a necessary investigation step that will help to understand the formation of primary oxide phases and indicate the initial oxidation behavior of the alloy. The SEM imaging in figures 10 & 11 showed the formation of two layers; one adherent to the surface and an outer spalled layer and the EDAX analyses reported that the upper layer contained manganese and Oxygen only while the inner layer contained Manganese, Chromium, Iron and Oxygen.

The cross sections and line EDAX showed in figure 12 indicate that the alloy had been oxidized externally and internally. By analyzing the line EDAX of 1 h sample it was clearly observed the formation of external manganese oxide containing some dissolved iron and at interface the concentration of chromium increases which supports the formation of Mn-Cr spinel. While, the line EDAX of 24 h sample show that the area which had been analyzed contains high concentration of chromium and manganese which is a part of the inner oxide.

Figure 7. Backscattered SEM imaging along with EDAX analyses of oxide surfaces at (a) 900 °C, (b) 1000 °C and (c) 1100 °C.
layer with the absence of outer layer due to spallation. Deep inside the alloy, the two high aluminum peaks shown in the figure indicate the formation of internal aluminum oxide precipitates.

3.4. General discussion
The SEM images of the oxide surfaces after 100 h at 900 °C, 1000 °C and 1100 °C show that the layers formed are uniform with no presence of spallation or cracks which indicate the formation of protective layers and explain the parabolic oxidation behavior of the alloy [23–25].
Looking through the cross-sectional SEM images, it is obvious that raising the oxidation temperature led to a significant increase in the thickness of manganese-oxides layer and formation of internal precipitates that is found only at 1000 °C and 1100 °C specimens. As at higher temperatures the outward diffusivity of manganese increases which support the formation of thick scale.
When comparing the scale-layer sequence shown through line-EDAX at all temperatures, they seem to form similar structure with different thickness values. It reveals that the external layer may be composed of two layers. The external layer consists of manganese oxides with some chromium and iron dissolved in that layer. The sudden increase of chromium content in inner layer may support the formation of MnCr$_2$O$_4$ spinel. This could be understood through the 1 and 24 h specimens that show the early stages of primary oxide layer formation, where XRD analysis detected the presence of MnCr$_2$O$_4$ spinel beneath the Mn$_3$O$_4$ outer layer [28].

The concentration of aluminum $\sim$ 5 at% in alloy was too low to form a continuous scale and led to the formation of internal oxide precipitates beneath the surface [29] that is detected through the line-EDAX where the Aluminum peaks suddenly increases. It was observed that the manganese content beneath the surface dramatically decreases while iron content increases. This can be explained due to the selective oxidation process of manganese.

4. Conclusions

The oxidation behavior of non equi-atomic alloy Al$_5$Cr$_{12}$Fe$_{35}$Mn$_{28}$Ni$_{20}$ high entropy alloy has been conducted. The study is carried at 3 different temperatures; 900 °C, 1000 °C and 1100 °C in atmospheric air isothermally for 100 h. The results of this investigation can be concluded into:

1. The oxidation behavior of alloy oxidized at 900 °C, 1000 °C and 1100 °C followed the parabolic rate law that was shown through the linear plot. While, the kinetics was obtained through the calculation of parabolic rate constants $K_p$ from the parabolic plot which equal to $3.34 \times 10^{-11}$, $8.23 \times 10^{-11}$ and $1.42 \times 10^{-10}$ g$^2$ cm$^{-4}$ sec, respectively and activation energy calculated equal 100.6 KJ mol$^{-1}$.

2. Oxidation of the alloy at all three temperatures led to the formation of duplex oxide layer; the external scale consisted of manganese oxides in accordance with the manganese-oxygen phase diagram; Mn$_3$O$_4$, Manganese (III) oxide (Mn$_2$O$_3$) and Manganese dioxide (MnO$_2$) and the internal layer is Mn-Cr-Fe spinel oxides.

3. It was found that when the samples were oxidized at 1000 °C and 1100 °C only the alloy was internally oxidized forming aluminum precipitates deep in the alloy.
4. The samples that were oxidized for 1 and 24 h scale analyses showed the formation of spalled upper layer consisted of manganese oxide (Mn₃O₄) which overlaps the Mn-Cr-Fe spinel layer and internal precipitates of aluminum oxide beneath the interface.

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The experimental aspect of this research was fully carried on in the Tabbin Institute for Metallurgical studies, Helwan, Egypt. It should be mentioned that the samples were prepared in Egypt-Japan University of Science and Technology, Alexandria, Egypt.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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