Oxidation and Corrosion properties of a Novel Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ High Entropy Alloy fabricated by Spark Plasma Sintering Technology

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Abstract
The need for new advanced high temperature materials is in high demand. High Entropy Alloy (HEAs) has been described to possess excellent mechanical oxidation and good corrosion resistance properties even far above the ambient temperature. Attempts are made in this research to study the corrosion, oxidation, microhardness and densification properties of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA produced by spark plasma sintering (SPS) for high temperature applications. In addition, the effects of SPS temperature (800, 900 and 1000°C) on the microstructure and phase formation of the developed HEA were reported. The microstructural modification and phases present were examined using the scanning electron microscope (SEM) equipped with the energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD) respectively. Ordered FCC and BCC systems were identified along with clearly defined crystal lattice along with Mo, Ti and Si rich regions were observed. No pores or cracks were observed from the microstructures. Densification of 98.8% accompanied with microhardness of 1445.29HV was achieved for both HEA at 1000°C. The Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA fabricated at 1000°C displayed a higher polarization value of 3477 Ω.

Keywords: High entropy alloys, oxidation, microhardness and corrosion

1. Introduction
The stability of materials in high temperatures is one of the most exotic characteristics that are required for manufacturing of high temperature applications. These components are required to have high thermo-mechanical fatigue resistance, excellent creep strength, hot corrosion and erosion resistance. Failure of the current market materials such as nickel based super alloys, titanium alloys and stainless steel due to high temperature oxidation, thermo-mechanical failure, high temperature wear and hot corrosion gives a room for alloy design
and properties optimization for new alloys [1-4]. These failures open room for more material development for high temperature application and high entropy alloys are a class of materials with promising properties. High Entropy Alloys (HEAs) are referred as an alloy containing 5 or more metallic elements where each of these alloying elements possesses varying concentration with the range between 5% - 35% [5-22]. These materials are a form of advanced alloy systems which displays substantial potential from the application and scientific perspective due to their numerous excellent properties as mentioned by [6, 20, 23-26]. It has been an established fact by so many researchers that Spark Plasma Sintering can readily develop materials of distinctive mechanical strength with homogenous small grains compared to the material developed by arc-melting process with inhomogeneous coarse grains [27-30]. Although spark plasma sintering offers unique advantages, it is still a difficult process to optimize the process parameters to control the formation of the final microstructure with little or no micro-cracks [31-34]. The development of AlCoCrFeNi high entropy alloy by spark plasma sintering was studied by Zhang et al. [35]. It was evident from the research findings that the AlCoCrFeNi HEA consists of a face-centred-cubic (FCC) phase and a duplex body centered (BCC) structure which was composed of spinodal modulated disordered and ordered BCC phases. The vickers hardness, yield strength, compressive strength, ultimate plasticity strain and fracture toughness of the HEA are reported to be 518 HV, 1262 MPa, 3228 MPa, 29.1% and 25.2 MPa m$^{1/2}$, respectively. Likewise, Kang et al., [10] studied ultra-high strength WNbMoTaV high-entropy alloys with fine grain structure fabricated by powder metallurgical process where the mechanical alloying behaviour, microstructure and mechanical strength mechanism of the HEA were investigated. The result of the experimental work depicted that the bulk sample of the WNbMoTaV HEA sintered at 1500°C showed ultra-high compressive yield strength of 2612 MPa with a failure strain of 8.8% at room temperature, respectively. In this work Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA was synthesized by means of SPS and corrosion, oxidation, microhardness and densification properties for the HEA were studied for potential high temperature applications.

2. Methodology

2.1 Spark plasma sintering

The ad-mixed powders of sample were emptied into the graphite mold of 40 mm (diameter) by 5 mm (height) dimension. The samples were subjected to the sintering process at varying
temperatures of 800°C, 900°C and 1000°C while keeping other parameters constant viz; the applied pressure of 50 MPa, the heating rate of 100°C/min, and the holding time of 8 min.

2.2 Density measurements of sintered HEA

The sintered samples were sandblasted to remove the graphite and other accomplished surface impurities that stacked onto the samples before the density measurements were recorded. The process took place by first weighing the sintered samples in air then immersed in water at room temperature to record the density. The density was repeatedly taken 5 times and an average was obtained for each sample.

2.3 Characterization of Sintered HEA

The sintered samples were sectioned to 5 mm x 5 mm smaller pieces subsequent to hot mounting using graphite resin powder and cold mounting using a liquid resin that solidifies at a higher rate in the presence of a drying agent. The samples were metallographically prepared by employing the grinding and polishing system using P320, 400, 600, 800 and 1000 grit sizes where an increase in grit size resulted in a clearer finish. Polishing then proceeded using a nylon cloth and a diamond suspension as a polishing agent.

2.3.1 Microstructural Investigation of the Developed HEA Samples

The microstructural modification and evolution of the developed alloys were examined using SEM. The grain size of the developed alloys was also measured by linear analysis on high magnification scanning electron micrographs followed by EDS. The phases formed in the sintered high entropy alloys were identified using an X-ray diffractometer. X-Pert High Score Plus software was employed to identify the background and peak-positions. Based on the peak positions and intensities; a search-match routine was performed to obtain the phases.

2.3.2 Microhardness testing

The hardness behavior of the sintered high entropy alloys was analysed on the polished samples using the EmcoTEST DURASCAN hardness testing machine. The indenting load of 100 g and a dwell time of 20s were used for this test. Diamond indents spaced at 0.002 mm apart were forced onto the material and the average-microhardness value was taken.

2.3.3 Electrochemical analysis
The electrochemical Potentiostat operates in a system of three electrodes; graphite connected with a black wire, the working electrode connected with a red wire and the reference electrode connected with a blue wire. The electrodes were submerged in a solution of 0.5M H₂SO₄ such that the test sample is fully submerged in the electrolyte solution. The Nova software was used to program the parameters. In this research work, start and stop potential of -1.5v and +1.5v, and the scan rate of 0.01 v/s was employed. The corrosion analysis was conducted to check the corrosion resistance prowess of the sintered alloys at varying temperature. Hence, corrosion rate, current density, corrosion potential, and polarization resistance of the developed HEAs alloy was extrapolated with tafel.

2.3.4 Thermal Stability Testing

PerkinElmer thermal gravimetric analyzer (TGA 4000) machine was employed to examine the oxidative behavior of the developed alloys. The samples were confined in the air atmosphere and heated from 25 to 900°C at a constant heating rate of 20°C/min.
3. Results and Discussion

3.1 Densification and Microhardness Results

Table 1 below present the density of the sintered HEAs alloys.

Table 1: Density measurements of the sintered samples

| Elemental composition (%) | Sintering temperature (°C) | Mass (g) | Theoretical density (g/cm³) | Density (g/cm³) | Relative density % |
|---------------------------|-----------------------------|----------|----------------------------|-----------------|--------------------|
| Al₅Ti₃₀Si₃₀Mo₁₅Ni₁₀       | 800                         | 27.79    | 4.55                       | 4.55            | 96.9               |
|                           | 900                         | 27.77    | 4.70                       | 4.61            | 98.1               |
|                           | 1000                        | 27.35    | 4.64                       | 4.64            | 98.8               |

The influence of the sintering temperature of high entropy alloy samples on the relative density is presented in table 1. The density result depicted that a high relative density of above 96.9% can be achieved for all sintered HEA samples at varying sintering temperatures. Moreover, it can be observed that the relative densification of the developed HEA increases with an increase in temperature. Al₅Ti₃₀Si₃₀Mo₁₅Ni₁₀ high entropy alloys sintered at 1000°C showed higher density of 98.8%, samples sintered at 900°C with 98.1% and at 800°C with 96.9% respectively. This is as a result of the powders being subjected to higher temperatures in which further melting of elemental powders is encouraged at a fixed applied force leaving no room for voids as the consolidated sample undergoes cooling stage.
Figure 1 present the mechanical behavior of the sintered HEA at varying temperatures in terms of the hardness mechanism using the vickers hardness tester. It is noteworthy that the material sintered at 1000°C had the maximum hardness of 1445.29 HV and the lowest hardness being 895.19 HV for the sample developed at 800°C. The observed high microhardness properties are due to the present of the aluminum which permit the formation of BCC phase and has stronger cohesive bonding with other inclusive elements. However, the cavities that were formed could be easily be infiltrated by the formation of new phases at the program sintering temperatures.

### 3.2 Phase evolution

The influence of the sintering temperature on the phase evolution was evaluated. Figure 2 below represent the XRD pattern of the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA developed by means of spark plasma sintering method at 800, 900 and 1000°C.
From the xrd spectrum results in Figure 2, both FCC and BCC solid phases were observed along with the intermetallics of NiTi$_3$ and TiSi$_2$ at all sintering temperatures. Miracle et al. Kale et al., 2017:362[36] declared that virtually all simple solid solution phase observed in HEA have either BCC or FCC structures. However, Zang et al. [21] attested that these structural phases can both exist in the HEA as observed from the xrd results. The intensified peaks for the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ material developed at 800°C are 41.4°, 45.3° and 47.6° with their inter-planer distance being 2.18 Å, 2.00 Å and 1.91 Å respectively. When sintered at 900°C the major diffraction peaks were identified at 40.7°, 47.8° and 73.6° with the inter-planer distance of 2.22 Å, 1.90 Å and 1.29 Å respectively. Lastly, the peak positions of the material sintered at 1000°C slightly differed from the previously mentioned material. The major diffraction peaks were observed to be 40.4°, 47.6° and 73.3°. It was witnessed that this material shared the same inter-planer spacing as material fabricated at 900°C. Zhang et al.[25] also stated that in general, single phase FCC systems shows highly ductile properties while single phase BCC systems is characterized with excellent yield strength due to a pronounced solid solution strengthening.

3.3 SEM/EDS Results

Figure 3 presents the representative microstructure accompanied by the EDS of the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA. All the fabricated HEA were sintered at 800, 900 and 1000°C with the heating rate of 100°C/min at a holding time of 8 min under a pressure of 50 MPa.
Figure 3: SEM-EDS morphology of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA sintered at; a) 800°C, b)900°C and c) 1000°C

From the micrographs presented, it can be depicted that no porous site or micro-cracks initiation due to stress induced can be seen in the material across all temperature ranges (800, 900 and 1000°C). This can be a result of even phase distribution as presented by the white (Mo-rich phase), dark grey, light grey and black phases. The increase in sintering temperature proves to have a significant effect on the crystal structures. As the temperature increases, crystal boundaries diminish and the TiSi phase increases. Si rich BCC phases (black) can be observed and is abundant in the material sintered at 900°C. Silicon in nature contains a large grain size and its presence in large amounts can segregate crystals causing weakness across crystal boundaries which can ultimately lower the hardness of the material.

**Electrochemical Studies**

Electrochemical studies were carried out on Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA. The samples were exposed in 0.5M Sulphuric acid. A Potentiostat device was used to obtain the results illustrated in the form of graphs below. The graphs shown below illustrate the corrosion resistance behavior of the HEA developed at varying temperatures.
Figure 4: Polarization curves of the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ of the HEA Developed at varying temperatures

The Tafel values from the corrosion data have been tabulated and are displayed in Table 2 below.

Table 2: Tafel corrosion data in Sulphuric acid

| Elemental composition (%) | Sintering temperature ($^\circ$C) | $E_{corr}$ (V) | $I_{corr}$ (A/cm$^2$) | C (R:mm/year) | PR (Ω) |
|--------------------------|----------------------------------|----------------|----------------------|----------------|--------|
| Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ | 800 | -0.36619 | 6.79E-05 | 0.009922 | 2986.54 |
|                           | 900 | -0.35041 | 4.18E-05 | 0.009187 | 3325.91 |
|                           | 1000 | -0.33489 | 7.98E-06 | 0.0051127 | 3477.01 |

Numerous investigative works pointed out that high entropy alloys are characterized with excellent corrosion resistance prowess [37-39]. This assertion emanated from the distinguish properties of HEA as a result of the individual intrinsic properties of the alloying elements. The corrosion behavior of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ in 0.5 M H$_2$SO$_4$ was studied. Figure 4
presents the corrosion performance of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ developed at 800, 900 and 1000°C. The polarization resistance outcome for all fabrication temperatures generally depicted excellent corrosion resistance in the aggressive acidic environment as compared to current commercial materials such as Ti6Al4V and stainless steel [34, 40, 41]. The result shows that the sample sintered at 1000°C reached the maximum polarization of 3477.01Ω. This could be attributed to the formation of the protective oxide layer of titania (TiO$_2$) and alumina (Al$_2$O$_3$) at higher temperature [42-44]. Furthermore, the good corrosion resistance behavior of the fabricated alloy could linked to the fact that sintering at higher temperatures encourages diffusion which hinders the corroding acid to penetrate the alloy [28]. Figure 5a and 5b show the SEM microstructures of the high entropy samples after corrosion test in 0.5M H$_2$SO$_4$. The SEM Images reveals a whitish oxide with black rich Si structures which are a result of deterioration caused by H$_2$SO$_4$. Formation of oxides along grain boundaries can be identified.

![Figure 5: micrographs of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ sintered samples a) 800°C and b) 1000°C after corrosion in 0.5 mol/L H$_2$SO$_4$](image)

**Oxidation Studies**

The oxidation behaviour of the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA sintered at difference conditions was carried out in high purity air. Figure 6 depicts the evolution of weight gain as the sample is heated at a constant rate of 20°C/min from ambient temperature to 900°C. The weight of all three samples were observed to remain relatively unchanged between ambient temperature and 650°C, this serves as proof of the stability (oxidation resistance) of the developed alloy.
below this temperature. However, these sintered specimens experienced a rapid increment in mass beyond the abovementioned temperature (particularly 650°C). This weight change can be due to the presence of some alloying elements with high affinity for oxygen, such as Ti, Al, Mo, Si and Ni which results in the formation of their oxides thus increasing the mass of the sample [34]. These newly evolved oxides are of paramount importance as they act as a protective oxide layer which serves the purpose of mitigating further oxidation.

Figure 6: The Oxidation Performance of the Fabricated Al15Ti30Si30Mo15Ni10 HEA

The rate at which each of these samples gained weight is different which is observed by differences in their steeps/gradient. The sample built at 1000°C, the highest sintering temperature explored herein, gain the largest amount in a short period compared to its counterparts which. The descending order of weight gain in the consolidated samples is sample sintered at 1000°C, 900°C and 800°C. This suggests that the samples built at the highest sintering temperature produced a comparatively thicker protective layer thus affirms it outstanding oxidation behavior. Figure 7a) and b) present the SEM micrographs of the
oxidized surface of the Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA fabricated at 800°C and 1000°C, respectively. The rough pattern of the oxide layer is clearly visible on these images.

Figure 7: SEM Micrographs of the Oxidized Surface of Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ Developed HEA at: a) 800°C and b) 1000°C

CONCLUSION

- Densification of 98.8% along with microhardness of 1445.29HV for Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ was achieved.
- The XRD results show that BCC and FCC systems were present in the HEA. Additional phases such as TiSi$_2$ and NiTi$_3$ were also found in Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ synthesized HEA developed at 1000°C.
- No pores and cracks were revealed from the microstructures evolved.
- The Al$_{15}$Ti$_{30}$Si$_{30}$Mo$_{15}$Ni$_{10}$ HEA developed at 1000°C revealed a higher polarization value of 3477Ω. This could be linked to the fact that sintering at higher temperatures encourages diffusion of particles which hinders the corroding acid to gain access into the lattice of the alloy.
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