Microstructure and anti-corrosion properties of near equiatomic Ti$_{25}$Si$_{25}$Al$_{20}$Mo$_{20}$Ni$_{10}$ High Entropy Alloy synthesized via Spark Plasma Sintering

L. R. Kanyane*, N. Malatji, A.P.I Popoola and O.S.I Fayomi

*Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa

Abstract

Materials operating at extreme conditions where they are exposed to corrosive environment can be realised in everyday applications. Suffer from corrosion due to acidic environment is still a challenge. Efforts have been made in material design to produce a suitable chemical plants material which can resist corrosion. High Entropy Alloys (HEAs) have been reported to exhibit enhanced mechanical and corrosion properties even at elevated temperatures. In this work, Al$_{20}$Ti$_{25}$Si$_{25}$Mo$_{20}$Ni$_{10}$ HEA with outstanding corrosion and microhardness properties was developed by means of spark plasma sintering technique (SPS) was synthesized. The effect of sintering temperature was investigated on microstructure, densification, microhardness and corrosion resistance properties of the synthesized alloy. The microstructural evolution and phase identification were characterized 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 grains along with Mo, Ti and Si rich regions. No cracks or initiation of stress were revealed from the microstructures. Maximum relative densities of 98.4% resulted in microhardness of 960.09 HV were achieved at sintering temperature of 1000°C. The Ti$_{25}$Si$_{25}$ Al$_{20}$Mo$_{20}$Ni$_{10}$ HEA fabricated at 1000°C displayed a higher polarization value of 3477 $\Omega$.

Key words: High entropy-alloys (HEAs), Corrosion, Spark plasma sintering (SPS)

1. Introduction

High entropy alloys remains potential candidates for replacement of current used nickel superalloys and Ti alloys due to their excellent properties such as good mechanical and electrochemical properties [1]. In comparison with traditional alloys, high entropy alloys consist of five or more principle elements in equi atomic and near equiatomic composition while traditional alloys contain single principle element [1-4]. Many reports stated that, severe lattice distortion, sluggish diffusion, cocktail effect and high configurational entropy are more responsible for their unique mechanical properties [5-9]. HEAs are also known to have stable crystal structures at high temperatures without precipitation due to simple solid solution body centered cubic (BCC), face centered cubic (FCC) and hexagonal closed-packed (HCP) which are mostly present in the alloy. BCC solid solutions phases are known for high strength as compared to fcc and hcp and the phase is more desirable for high temperature applications where high strength, creep and fatigue resistance are required [10, 11].
Different HEAs are developed to meet several industrial and engineering applications. This gives a room to explore more on HEAs with improved properties as compared to the developed alloys. Mohanty et al., [12] developed multicomponent AlCoCrFeNi HEA using spark plasma sintering. The results showed that hardness of the sample increases with sintering temperature. The fabricated AlCoCrFeNi alloy revealed the presence of fcc phase along with bcc structure. Kang et al., [13] synthesized WNbMoTaV HEA which presented fine grain structure developed by powder metallurgical process. WNbMoTaV HEA proved to have outstanding mechanical properties which were attributed to intrinsic solid solution strengthening, with the combined effect of grain boundary strengthening and interstitial solid solution strengthening. The work aim to investigate microhardness, densification, and corrosion properties of Al20-Ti25Si25Mo20Ni10 HEAs processed via spark plasma sintering.

2. Experimental Setup
A tubular shaker-mixer was run for 8 hours at a speed of 49 rpm to combine the selected elemental powders to obtain a homogenous powdered mixture. The ad-mixed powders of sample A was poured inside a 40 mm x 5 mm mold lined with graphite paper. The samples were sintered at varying temperatures namely, 800°C, 900°C and 1000°C. The sintering process took place at the following conditions; (1) heating rate of 100°C/min (2) applied pressure of 50 MPa (3) holding time of 8 min for each powdered sample. After all the samples were sandblasted to remove the graphite that adhered onto the samples, density measurements were recorded. A total of five density measurements were recorded and averaged for each sample.

The sintered samples were sectioned hot mounted prior to metallography. The samples were then subjected to coarse and fine grinding using P320, 400, 600, 800 and 1000 grit sizes and polished. The microstructure of Ti25Si25 Al20Mo20Ni10 was characterized using scanning electron microscope (SEM). XRD was utilized to identify the phases present in the alloy and present phases were revealed using X-Pert High Score Plus software.

The Vickers Microhardness values of the developed HEA were measured using the Emco TEST DURASCAN hardness testing machine with the Ecos workflow ultramodern software as an accompaniment. The indenting load of 100kgf and a dwell time of 15s were used for this test.

The corrosion resistance properties of the samples were studied in 0.5M H2SO4. The Nova program was used to set the parameters. It was set to run the corrosion test as follows: the highest current at 1mA, lowest current at 100mA, start potential of -1.5v, stop potential of 1.5v and the scan rate at 0.01v/s. When the test was complete, a polarization graph of potential versus current density was plotted.

3. Result and Discussion
The density measurements of the HEA sintered samples were recorded as illustrated in Table 1 below.

| Elemental composition (%) | Sintering temperature (°C) | Mass (g) | Theoretical density (g/cm³) | Density (g/cm³) | Relative density % |
|--------------------------|---------------------------|----------|----------------------------|----------------|-------------------|

Table 1: Density measurements of sintered HEAs
SEM/EDS Results

Figure 1 shows the morphological evolution of the developed Ti$_{25}$Si$_{25}$ Al$_{20}$Mo$_{20}$Ni$_{10}$ HEA. The effect of spark plasma sintering temperature on the morphological evolution was investigated. There are no significant changes on surface morphology at various sintering temperature. The fabricated HEA shows white (Mo rich phase), black precipitated spots (Si rich phase) and gray (Ti rich phase) contrast phases. The micrographs appearance also shows no form of cracks or initiation of stress at all sintering temperatures. Smaller grain size can be seen on the HEA sintered at 1000°C (Figure 1c) with thicker grain boundaries which promotes the increase in the TiSi$_2$ phase rim as proved by the EDS.

**Figure 1: SEM-EDS morphology of Ti$_{25}$Si$_{25}$ Al$_{20}$Mo$_{20}$Ni$_{10}$ HEA sintered at a) 800°C b) 900°C and c) 1000°C.**

X-Ray Diffraction Results

Figure 2 below represents the XRD pattern of the Ti$_{25}$Si$_{25}$Al$_{20}$Mo$_{20}$Ni$_{10}$ HEA fabricated by SPS method at 800, 900 and 1000°C. It is observed from the spectrum results that fcc, bcc solid solution phases were present in the synthesized alloy while intermetallics of NiTi$_3$, TiSi, and Ni$_2$Si$_2$ were also presented in the fabricated alloy at all sintering temperatures. Rani [14] stated that all simple solid solution phase observed in HEAs have either bcc or fcc structures. However, Authors [7, 9, 15] added that these structures can both exist in the HEA. The major diffraction peaks for the Ti$_{25}$Si$_{25}$Al$_{20}$Mo$_{20}$Ni$_{10}$ material fabricated 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. 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°. A single phase fcc systems tend to display highly ductile properties while single phase bcc systems exhibit increased yield strength due to a pronounced solid solution strengthening.
Density and Microhardness Results
From figure 3a, high relative density of above 94.7% was achieved for all fabricated Ti25Si25Al20Mo20Ni10 HEA at varying sintering temperatures of 800, 900 and 1000°C. It is clear an increase in densification of fabricated HEA result in an increase in temperature. HEA sintered at 1000°C presented a supreme densification of 98.4, followed by 95.7 and 94.7% respectively as sintering temperature decreases. This could be attributed to high particle to particle diffusion that takes place at high sintering temperature [16]. From Figure 3b it is observed that the highest HV was found to be 781 HV and the lowermost HV value was 610HV. This presence of bcc phase has been reported by several authors to exhibit excellent mechanical properties which could be the reason for high microhardness properties of the alloy. Furthermore, hard intermetallic phase of NiTi3 is responsible for high microhardness properties of the developed HEA [17].

Electrochemical Studies
Figure 4 present electrochemical studies of Al20Ti25Si25Mo25Ni10 HEA. The test was achieved in 0.5M Sulphuric acid. Numerous works proved that HEAs own good corrosion resistance properties [4, 18, 19]. The alloying elements of 5 or more elements gives HEAs advantages under corrosive environment. The corrosion behavior performance of Al20Ti25Si25Mo20Ni10 at 800, 900 and 1000°C generally show outstanding corrosion resistance. It is clear that sample sintered at 800°C presented low current density of 1.09E-06 A/cm² with a potential of -0.49V. While HEA sample developed at 1000 °C displayed potential slightly high potential -0.47V and a current density of 1.87E-03 A/cm². The good corrosion resistance for the alloy could be a result of a protective oxide film of Al and Ti as observed in Figure 5.
Figure 4: Polarization curves of the Al$_{20}$Ti$_{25}$Si$_{25}$Mo$_{20}$Ni$_{10}$ HEA

Figure 5: micrographs of Ti$_{25}$Si$_{25}$ Al$_{20}$Mo$_{20}$Ni$_{10}$ sintered samples a) 800°C and b) 1000°C after corrosion in 0.5 mol/L H$_2$SO$_4$

Conclusions

- An increase in sintering temperature results an increase in the relative density of the fabricated HEA samples. A maximum relative density of 98.4 and 98.8% for Al$_{20}$Ti$_{25}$Si$_{25}$Mo$_{20}$Ni$_{10}$
- XRD results revealed that BCC and FCC systems were present in the HEAs. Additional phases such as TiSi, Ni$_2$Si$_2$ and NiTi$_3$ were also found in the Al$_{20}$Ti$_{25}$Si$_{25}$Mo$_{20}$Ni$_{10}$.
- No cracks or initiation of stress were observed from the microstructural images.
- The Al$_{20}$Ti$_{25}$Si$_{25}$Mo$_{20}$Ni$_{10}$ HEA fabricated at 800°C displayed good corrosion resistance properties.

Acknowledgement

The authors would like to acknowledge the following

- Tshwane University of Technology and the Department of Chemical Metallurgical and Materials Engineering, South Africa.

References

1. Yang, X. and Y. Zhang, Prediction of high-entropy stabilized solid-solution in multicomponent alloys. Materials Chemistry and Physics, 2012. 132(2-3): p. 233-238.
2. Varalakshmi, S., M. Kamaraj, and B. Murty, Processing and properties of nanocrystalline CuNiCoZnAlTi high entropy alloys by mechanical alloying. Materials Science and Engineering: A, 2010. 527(4-5): p. 1027-1030.
3. Wang, W.-R., et al., Effects of Al addition on the microstructure and mechanical property of Al$_x$CoCrFeNi high-entropy alloys. Intermetallics, 2012. 26: p. 44-51.
4. Wu, C., et al., *Phase evolution and cavitation erosion-corrosion behavior of FeCoCrAlNiTi high entropy alloy coatings on 304 stainless steel by laser surface alloying*. Journal of Alloys and Compounds, 2017. 698: p. 761-770.

5. Yeh, J.-W., et al., *Formation of simple crystal structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V alloys with multiprincipal metallic elements*. Metallurgical and Materials Transactions A, 2004. 35(8): p. 2533-2536.

6. Zhang, W., P.K. Liaw, and Y. Zhang, *Science and technology in high-entropy alloys*. Science China Materials, 2018: p. 1-21.

7. Zhang, Y., et al., *Guidelines in predicting phase formation of high-entropy alloys*. Mrs Communications, 2014. 4(2): p. 57-62.

8. Zhang, Y., et al., *Minor alloying behavior in bulk metallic glasses and high-entropy alloys*. Science in China Series G: Physics, Mechanics and Astronomy, 2008. 51(4): p. 427-437.

9. Zhang, Y., et al., *Solid-solution phase formation rules for multi-component alloys*. Advanced Engineering Materials, 2008. 10(6): p. 534-538.

10. Cantor, B., et al., *Microstructural development in equiatomic multicomponent alloys*. Materials Science and Engineering: A, 2004. 375: p. 213-218.

11. Chen, S.-K., *Electrochemical Passive Properties of AlxCoCrFeNi (x= 0, 0.25, 0.50, 1.00) High-Entropy Alloys in Sulfuric Acids*, in Corrosion Resistance. 2012, InTech.

12. Mohanty, S., et al., *Powder metallurgical processing of equiatomic AlCoCrFeNi high entropy alloy: microstructure and mechanical properties*. Materials Science and Engineering: A, 2017. 679: p. 299-313.

13. Kang, B., et al., *Ultra-high strength WNbMoTaV high-entropy alloys with fine grain structure fabricated by powder metallurgical process*. Materials Science and Engineering: A, 2018. 712: p. 616-624.

14. Rani, R.U., et al., *DESIGN AND STRUCTURAL ANALYSIS OF EXHAUST ENGINE VALVE WITH HIGH ENTROPY ALLOYS*. 2018.

15. Srijharitha, R., B. Murty, and R.S. Kottada, *Phase formation in mechanically alloyed AlxCoCrCuFeNi (x= 0.45, 1, 2.5, 5 mol) high entropy alloys*. Intermetallics, 2013. 32: p. 119-126.

16. Makena, M.I., et al., *Effect of sintering parameters on densification, corrosion and wear behaviour of Ni-50Fe alloy prepared by spark plasma sintering*. Journal of Alloys and Compounds, 2017. 699: p. 1166-1179.

17. Adesina, O., et al., *A STUDY ON SCAN SPEED RELATIONSHIP WITH MICROSTRUCTURAL EVOLUTION, PHASE COMPOSITION AND MICROHARDNESS OF Ni-CONTAINING INTERMETALLIC COATINGS ON Ti–6Al–4V USING LASER CLADDING TECHNIQUE*. Surface Review and Letters, 2018. 25(08): p. 1950035.

18. Shi, Y., et al., *Corrosion of AlxCoCrFeNi high-entropy alloys: Al-content and potential scan-rate dependent pitting behavior*. Corrosion Science, 2017. 119: p. 33-45.

19. Lee, C., et al., *Effect of the aluminium content of AlxCrFe1. 5MnNi0. 5 high-entropy alloys on the corrosion behaviour in aqueous environments*. Corrosion Science, 2008. 50(7): p. 2053-2060.