Feasibility Study of High Entropy Alloy (HEA) Production
Containing Al–Cr–Cu–Fe–Ni by Using Direct Electric–Arced Method

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Abstract

High entropy alloys (HEAs) are novel materials containing more than five elements in equimolar ratio compositions providing complex and versatile microstructures and mechanical properties with different conceptual from previous alloy materials. However, preparation and production methods of HEA are difficult melting techniques and not economically reasonable. Many previous researches produce HEA specimens by using high purity raw materials and sophisticated methods such as laser metal deposition and spark plasma sintering.

Objective: The aim of this study was to propose the method for HEA production by using the simple melting method combination with the locally available raw materials producing HEAs serving applications those requiring good combination of strength and hardness.

Methods: Main elements used for producing HEA specimen in this study were consisting of Al, Cr, Cu, Fe and Ni in equimolar concentration. HEA samples were prepared in several melting weight of 200 g, 100 g, 50 g, 40 g, 30 g and 20 g which each condition was melted by using direct arc method in refractory crucible.

Results: Microstructural investigation by optical microscope and scanning electron microscope (SEM) observing from 100 g, 40 g and 20 g samples showed highly segregate dendritic structure of the AlCrCuFeNi HEA. As-cast structure revealed lamellar matrix structure consisting several alloy phases including Cu-Al rich phase, Fe-Cr-Ni and Cu-Al-Ni-Fe phases and rod-like chromium carbide dispersed in the matrix structure. Large amount of carbide presented in all samples especially in 100 g HEA sample due to carbon dissolved from graphite electrode during direct arc-melting combining with chromium from raw materials resulted in chromium carbide. Microstructures of small weight samples showed lower amount of carbide formation as the shorter arc melting time which limiting the carbon from electrode dissolving into the melt. Microhardness test results of all HEA samples were superior to other commercial alloys. The localized microhardness test of 50 g HEA as-cast sample showed the highest hardness data in the range of 707.4 – 819.9 HV1 which was much higher than those of hot-work tool steels.

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1. Introduction

HEAs are "those composed of five or more principal elements in equimolar ratios" (Yeh et al, 2004). HEAs have caught attention from many researchers for their unique properties and versatile applications in various industries (Murty et al, 2014). These properties were proposed to be from the four-core effect: high-entropy effect, sluggish diffusion effect, severe lattice distortion effect, and cocktail effect (Yeh, 2006). A number of criteria has to be met in order for solid solution HEAs to be form which are compiled from empirical data and summarized in Table 1 (Guo, 2015).

Table 1. Guideline for material selection conforming to the solid solution HEAs.

Variable	Criteria
Entropy of mixing: (ΔS_{mix})	Max value
Enthalpy of Mixing: (ΔH_{mix})	-10 to 5 kJ/mol
$\dfrac{(T_m \Delta S_{mix})}{(\Delta H_{mix})}$	≥ 1.1
Atomic radius mismatch: δ	≤ 6.6%
Valence Electron Concentration: VEC	≥ 8 for FCC, <6.87 for BCC

Where T_m is given by

$$T_m = \sum_{i=1}^{n} c_i (T_m)_i$$

and $(T_m)_i$ was the melting point for the ith component of the alloy.

The most of recent methods used for producing of HEAs were prepared by melting the high purity materials that was usually 99% purity in a vacuum chamber using heat from an arc generated between the electrode and materials (Butler, & Weaver, 2017). On the other hand, other method such as spark plasma sintering prepared by using powder metallurgy (Zhou et al, 2019) and laser metal deposition (Chen et al, 2017) have been the successful techniques for producing HEAs as well. However, the current processes are costly and requiring high purity materials which are not economically suitable. Therefore, this research work aims to produce HEA using a simpler method and economically available raw materials.

In this work, we used AlCrCuFeNi as the 5 main components for producing HEA samples by using direct-arced melting method in order to provide the technique for HEA production that was based on the availability and economically reasons. This HEA system is similar to alloy composition and dual phase structure of FCC and BCC which has been reported that the hardness increasing with higher aluminium content (Li et al, 2008). The FCC-BCC dual phase structure of AlxCoCrFeNi alloy has been reported in higher yield strength than its single-phase FCC structure without loss of its ductility due to the interphase boundaries in its eutectic lamellar structure (Gangireddy et al, 2019). Therefore, the AlCrCuFeNi alloy system in this study will be expected to contain the FCC-BCC dual phase lamellar structure with high strength and good ductility as the previous literatures.

2. Experimental Procedure
2.1 Preparation of HEA samples

Aluminium rod, copper rod, SR24 steel rod, Ferrochromium (FeCr) and Nickel ingot were used as raw materials for producing HEA alloy. The chemical compositions of raw materials were summarized in Table 2. In this study, the raw materials were prepared in equimolar concentration of 5 elements in the system of Al-Cr-Cu-Fe-Ni alloy.

Table 2. Chemical composition of raw materials for producing HEA alloy.

Raw Materials	%Al	%Si	%Fe	%Cu	%Mn	%Cr	%Ni	others
Al rod	89.5	0.589	>7.20	>0.480	0.880	>0.30	>0.144	0.295
SR24 steel rod	0.017	1.01	96.1	-	0.880	0.321	-	0.972
Cu rod	-	-	-	99.9	-	-	-	0. 1
Ferrochromium ingot	-	0.001	34.48	-	-	69.52	-	-
Nickel ingot	-	-	-	-	-	-	99.0	0.1

Direct arc method was applied for melting HEA samples by using an AC arc welding machine MID-500T model with carbon electrodes arc in refractory crucible as shown in Figure 1. During melting process, HEA samples were prepared by varying the melting weights as 200 g, 100 g, 50 g, 40 g, and 30 g in order to observe the microstructural homogeneity of HEA alloy in each melting condition that constraint with melting energy limitation of the equipment.

2.2 Microstructural and mechanical properties

Microstructural examination of the AlCrCuFeNi HEA samples were investigated by optical microscope and field emission scanning electron microscope (FE-SEM), Auriga Zeiss. Preliminary evaluation of the microstructural composition of phases was analyzed by using energy dispersion X-ray spectroscopy (EDS) equipped in FE-SEM. Micro-Vickers hardness test was used for preliminary evaluating the mechanical property of the HEA samples by applying a load of 1 kgf (HV1) for testing. The properties results were compared to other high strength commercial alloys.

3. Results and discussion
3.1 Microstructural observation of as-cast AlCrCuFeNi HEA alloy

The as-cast of AlCrCuFeNi alloy samples with different melting weights are shown in Figure 2. The raw materials of smaller weight samples were well mixed during melting process and resulted in more uniform structure of AlCrCuFeNi HEA alloy as clearly seen on 100 g sample in Figure 2(b) comparing with 200 g sample in Figure 2(a).

All samples were etched with Villella's before microscopic and SEM examination. At 100x and 400x magnification of as-cast microstructures in Figure 3 consisted of dendritic structure due to the chemicals segregations during solidification which was normally found in high alloy materials. SEM micrograph of as-cast samples in Figure 4 revealed the lamellar structure matrix with large metal carbide as rod-like structure (grey) which confirmed by SEM-EDS point scan in Figure 5 and 7 and SEM-EDS map scan in Figure 6. The compositional analysis from EDS suggested that the carbide particles would be M_7C_3 (M = Fe,Cr). The hexagon M_7C_3 carbide particles were mostly observed in the 100 g ingot but they were not found in the 20 g sample (comparing in Figure 3 and Figure 4). For the large samples, the longer arc melting time would allow the higher carbon content from graphite electrode dissolving into the melt and combining with Cr in the melt resulting in more amount of those polygonal carbide particles.
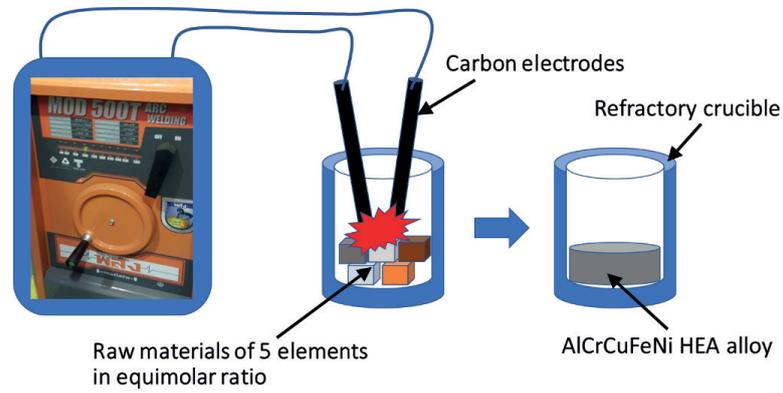
Fig 1. Schematic diagram of direct arc melting trial process to produce HEA alloy in this study.

(a) 200 g sample **(b) 100 g sample**

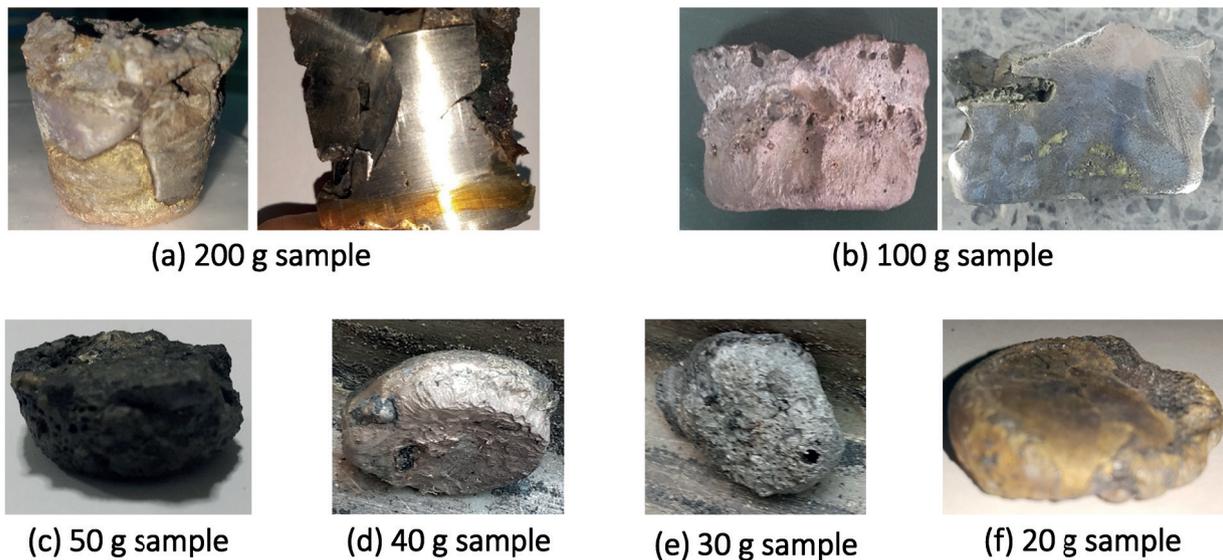**(c) 50 g sample** **(d) 40 g sample** **(e) 30 g sample** **(f) 20 g sample**

Fig 2. As-cast samples of AlCrCuFeNi HEA alloy in various trial melting weights of (a) 200 g, (b) 100 g, (c) 50 g, (d) 40 g, (e) 30 g and (f) 20 g samples.
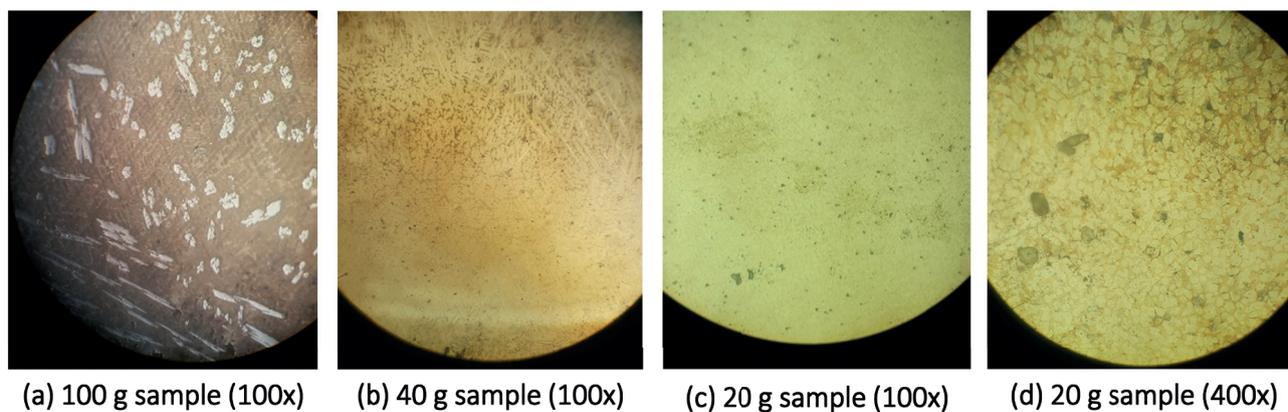

(a) 100 g sample (100x) **(b) 40 g sample (100x)** **(c) 20 g sample (100x)** **(d) 20 g sample (400x)**

Fig 3. As-cast microstructures of (a) 100 g, (b) 40 g, (c) 20 g sample at 100x magnification and (d) 20 g samples at 400x magnification.
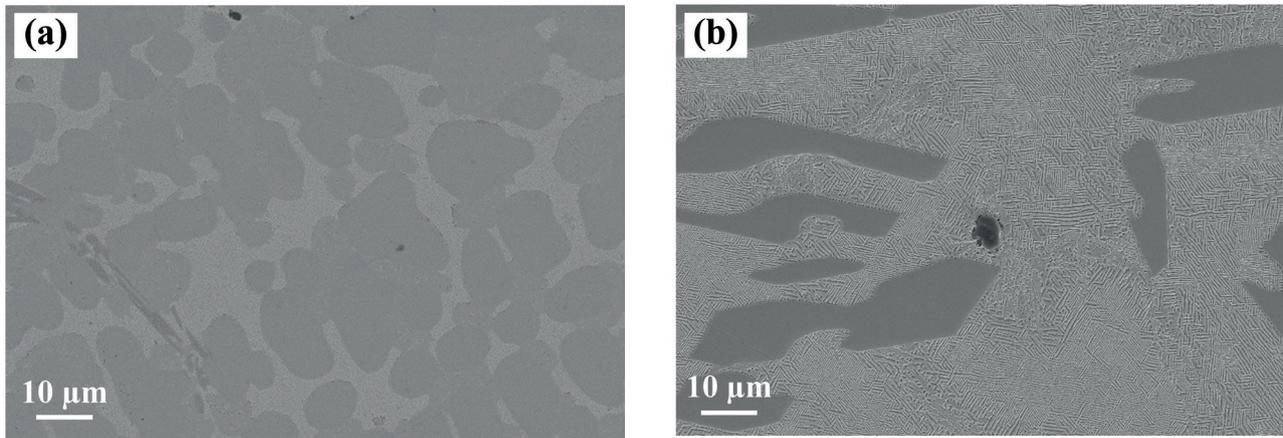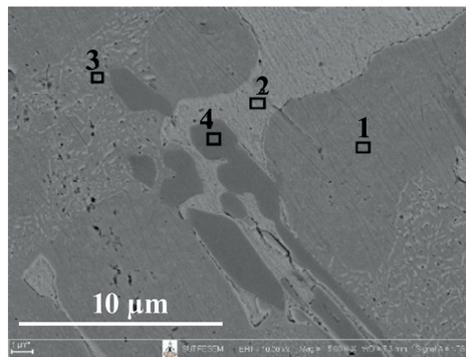
Fig 4. Backscattered electron micrograph of as-cast structures of (a) 20 g sample and (b) 100 g sample were observed chromium carbide (rod-like region) in the lamellar structure matrix.

Point	At atomic%					
	Fe	Ni	Cr	Cu	Al	C
1	20.44	6.27	21.67	-	2.93	47.56
2	5.40	-	2.99	23.09	4.47	64.05
3	5.05	20.97	-	13.34	9.88	50.80
4	-	-	42.52	-	-	57.48

Fig 5. SEM-EDS point scan results of each phase areas in as-cast microstructure of 20 g sample.

SEM-EDS point scan results of 20 g HEA sample showed several phases in different chemical compositions in Figure 5. At point 1, the elemental compositions analysis suggested that it was Fe-Cr-Ni alloy phase. Cu-rich alloy phase and Ni-Cu-Al alloy phase found at point 2 and point 3, respectively. The chromium carbide phase (rod-like structure) was presented at point 4. The chemical compositions distribution that characterized by SEM-EDS map scan result of the 40 g HEA sample shown in Figure 6 was corresponding to the elemental distribution as earlier discussed. In addition, the SEM-EDS point scan result of 100 g HEA sample in Figure 7 also observed Cu-rich Ni-Al-Fe alloy phase at point 2 and chromium carbide at point 1 which similar to the result observing in 20 g and 40 g HEA samples microstructure. The results in figure 7 at point 3 found some small phase consist mainly of Al and N which nitrogen in air might be reacting with aluminum during melting to form aluminum nitride embedded in the matrix. Moreover, the EDS linescan composition of lamellar matrix structure in the 100 g HEA sample in Figure 8 showed that the darker band region in the lamellar structure contained Cu-rich phase while the brighter band region

contained Cu-Al rich alloy phase which these result similar to the compositions of phase in the matrix of HEA samples shown in Figure 5 to Figure 7. As a result of HEA melting data, the smaller weight samples needed shorter applied arc time. This would lead the melt not thoroughly mixed and caused varying localized concentration of the main elements. For larger weight samples, the longer arc time would introduce more amount of carbon from graphite electrode dissolving into the melt resulted in the more chromium carbide particles in the HEA microstructure.

Therefore, further work would be recommended using tungsten electrode instead of the carbon electrode to prevent carbide formation from dissolved carbon into the HEA melt during the melting process. Moreover, in order to prevent the melts interacting with gases in ambient atmosphere, the inert gas purging would be applied to cover the melt surface.
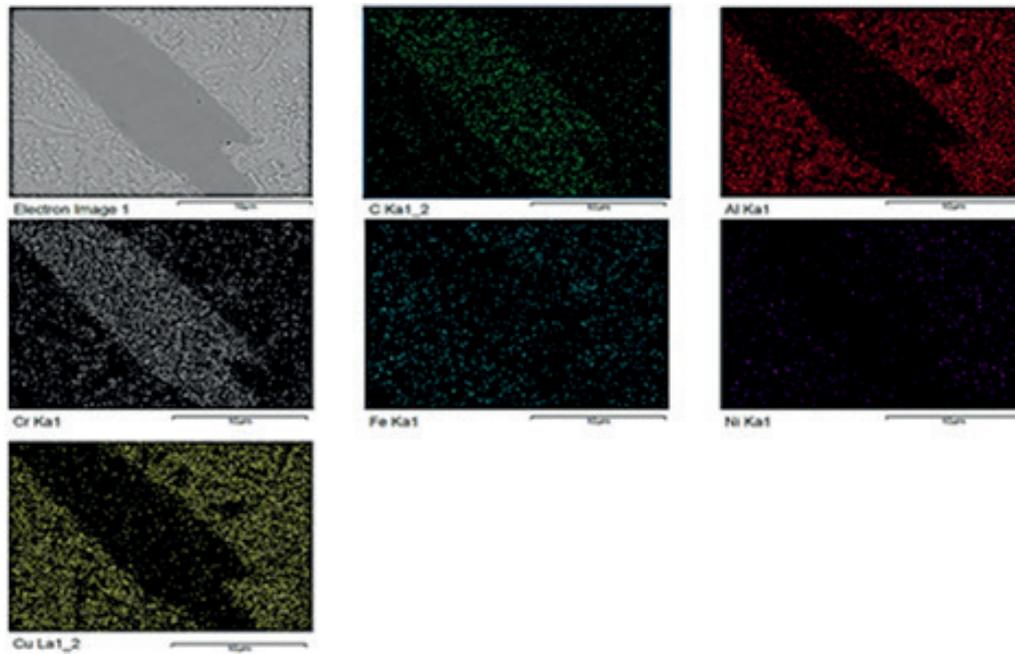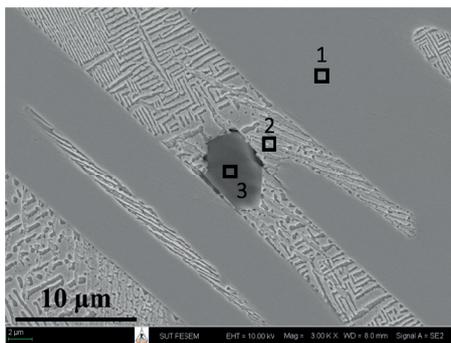

Fig 6. SEM-EDS mapping scan for the as-cast microstructure of the 40 g HEA sample.

Point	At atomic%							
	Fe	Ni	Cr	Cu	Al	C	N	O
1	18.14		51.79			30.07		
2	10.00	23.53		48.10	17.21			
3					42.77		53.59	3.64

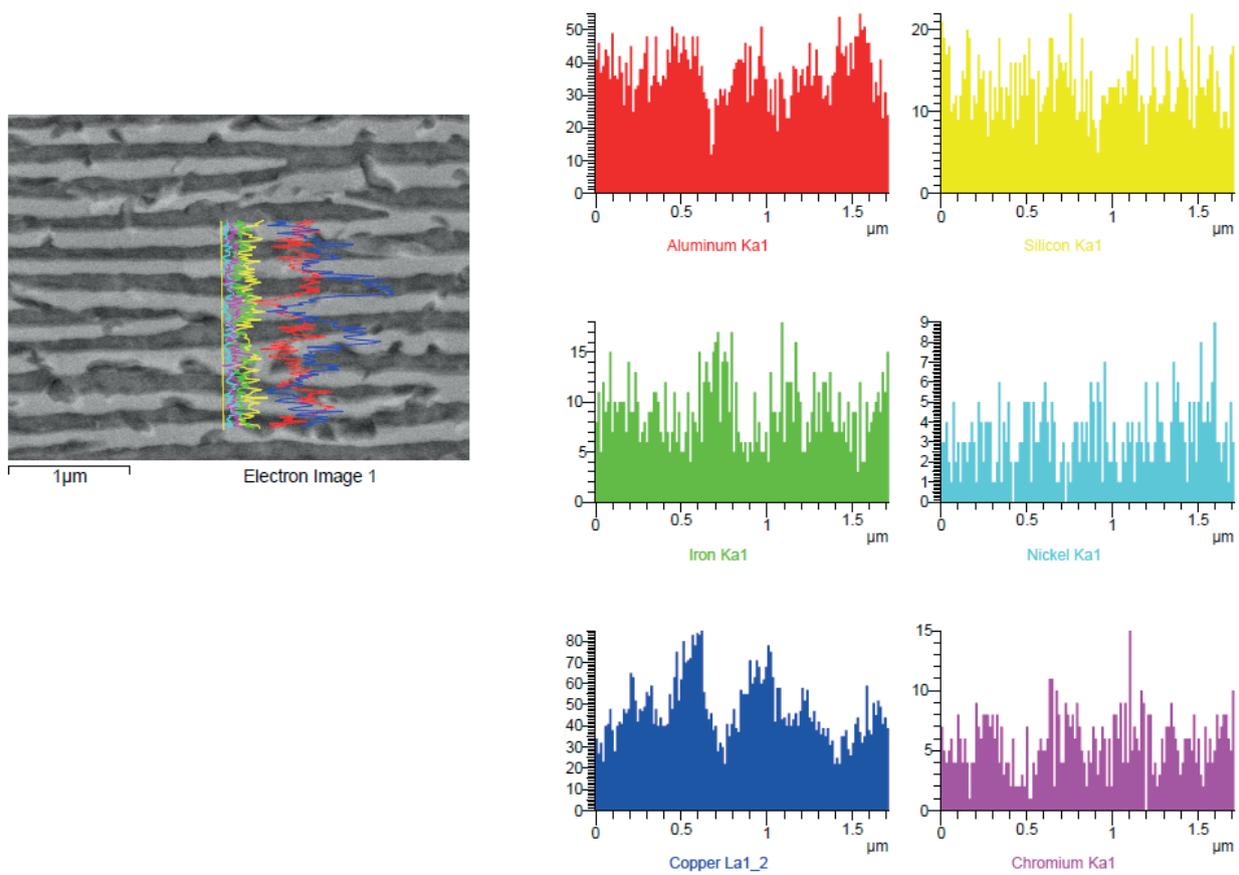**Fig 7.** SEM-EDS point scan results in as-cast microstructure of 100 g HEA sample.

Fig 8. SEM-EDS line scan results for lamellar structure (matrix) of 100 g HEA sample.
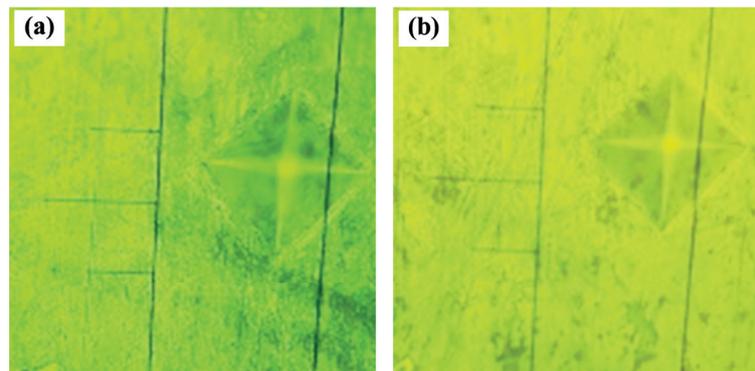

Fig 9. Indentation of microvickers hardness test results in microstructure of 50 g sample in different areas that shown hardness of 707.4 $HV_{1.0}$ in (a) and hardness of 819.9 $HV_{1.0}$ in (b).

Table 3. Hardness data of the HEA samples comparing with other commercial steels.

Conditions	HV$_{0.1}$	HV$_{0.2}$	HV$_{1.0}$	HV$_{5.0}$	HV$_{30}$
20 g sample			451.6 - 655.2		
40 g sample			375.1 - 523.7		
50 g sample			707.4 – 819.9		
200 g sample			419.7 - 515.5		
SS316L	200				140
Carbon steel				55 - 120	
H13 (before heat treatment)		200			
H13 (conventional heat treatment)		600			

* 100 g sample was used for SEM and XRD (not included in this report) characterization and   sample was not good enough for hardness testing

3.2 Hardness data of as-cast AlCrCuFeNi HEA alloy

The micro-vickers hardness test results of AlCrCuFeNi HEA alloy samples in as-cast condition comparing to others commercial alloys are shown in Table 3. For microhardness testing, chromium carbide phase region had to be avoided during the micro-indentation test. Hardness data of all HEA samples were significantly higher than other commercial alloys, especially H13 hot work tool steel in conventional heat treatment condition (quenching and tempering). HEA sample of 50 g had the highest mean hardness over of all the samples. The region of indentation and hardness value of 50 g HEA sample are shown in figure 9. The reason for 50 g HEA sample higher hardness value than others is unclear. The hardness of 20, 40 and 200 g HEA samples showed similar hardness even though 200 g sample which microstructure containing lamellar structure matrix and large amount of carbide that was as same as the 100 g sample microstructure due to localized hardness test area not including the effect of hardness of chromium carbide phase. As a result of preliminary evaluating the hardness property, it might be applying this alloy to create the HEA materials or multiphase alloy with novel properties for high hardness and high strength such as tool materials and structural applications.

4. Conclusion

In this preliminary study for producing AlCrCuFeNi HEA materials by using direct arc technique can be achieved to get homogeneous melt samples for small weight sample up to 100 g due to limitation of the equipment power source used in this work which only allowed to prepare the samples in the experimental scale.

The microstructural characterization of the AlCrCuFeNi HEA samples in this study mainly observed the lamellar matrix structure consisted of Fe-Cr-Ni alloy phase and Cu-rich-Al alloy phase, rod-like chromium carbide and polygonal M7C3 dispersed in the matrix due to the carbon from graphite electrodes dissolved into the melt during arc-melting operation.

The hardness data of these HEA alloy showed clearly superior hardness property to other commercial alloy materials which can be developed for the application that require high hardness and high strength.

For the further work, the interested topic for microstructures and properties of the AlCrCuFeNi HEA alloy improvement is to homogenize the as-cast structure and tailoring the microstructures and mechanical properties through thermal treatment.

The effect of chromium carbide on the samples mechanical properties and ways to manipulate it size and concentration in the as-cast structure are also topics of interest.

5. Acknowledgement

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