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Copyright HolderName	The Minerals, Metals & Materials Society	
Corresponding Author	Family Name	**Dada**
	Particle	
	Given Name	**Modupeola**
	Prefix	
	Suffix	
	Role	
	Division	Chemical, Metallurgical and Materials Engineering
	Organization	Tshwane University of Technology
	Address	Pretoria, South Africa
	Email	dadadupeola@gmail.com
Author	Family Name	**Popoola**
	Particle	
	Given Name	**Patricia**
	Prefix	
	Suffix	
	Role	
	Division	Chemical, Metallurgical and Materials Engineering
	Organization	Tshwane University of Technology
	Address	Pretoria, South Africa
	Email	PopoolaAPI@tut.ac.za
Author	Family Name	**Mathe**
	Particle	
	Given Name	**Ntombi**
	Prefix	
	Suffix	
	Role	
	Division	
	Organization	Council for Scientific and Industrial Research
	Address	Pretoria, South Africa
	Email	NMathe@csir.co.za
Author	Family Name	**Pityana**
	Particle	
	Given Name	**Sisa**
	Prefix	
	Suffix	

	Role	
	Division	
	Organization	Council for Scientific and Industrial Research
	Address	Pretoria, South Africa
	Email	SPityana@csir.co.za
Author	Family Name	**Adeosun**
	Particle	
	Given Name	**Samson**
	Prefix	
	Suffix	
	Role	
	Division	Metallurgical and Materials Engineering
	Organization	University of Lagos
	Address	Akoka, Nigeria
	Email	samsonoluropo@yahoo.com
Author	Family Name	**Lengopeng**
	Particle	
	Given Name	**Thabo**
	Prefix	
	Suffix	
	Role	
	Division	
	Organization	Council for Scientific and Industrial Research
	Address	Pretoria, South Africa
	Email	TLengopeng@csir.co.za

Abstract	Laser additive manufacturing is a direct energy deposition process which manufactures components from 3D model data in progressive layers until a whole part is built as opposed subtractive manufacturing. However, during the procedure, the deposits are subjected to rapid thermal stresses which adversely impact the integrity of the built component. High entropy alloys are materials with complex compositions of multiple elements. Traditionally, these alloys are fabricated using casting and other machining processes, with a recent interest in the use of laser deposition as a possible manufacturing process. To optimize process parameters of high entropy alloys melted on a steel plate, the influence of preheating temperature on the overall quality, microstructure and hardness behaviour of the alloys for aerospace applications were investigated. In this research, 9 samples of AlCoCrFeNiCu and AlTiCrFeCoNi high entropy alloys were fabricated using different laser parameters. The phases, chemical composition, micro-hardness and structural morphologies were characterized with XRD, EDS, Vickers Microhardness tester and SEM respectively before and after preheating the base plates at 400 °C. Experimental results show extensive cracking on all the samples without preheating while after preheating all samples were observed to be crack-free. Although, there were no variations on the dendritic structures in the optical micrographs with and without preheating temperature, there were notable changes in the phases and hardness behaviour of the alloys showing that preheating the base plate from 400 °C significantly influences the mechanical properties of additive manufactured high entropy alloys and contributes to the elimination of cracks induced by thermal stresses.

Keywords	Base plate preheating - High entropy alloys - Laser additive manufacturing - Optimal parameters - Thermal stresses

Fabrication and Hardness Behaviour of High Entropy Alloys

Modupeola Dada, Patricia Popoola, Ntombi Mathe, Sisa Pityana,
Samson Adeosun and Thabo Lengopeng

Abstract Laser additive manufacturing is a direct energy deposition process which manufactures components from 3D model data in progressive layers until a whole part is built as opposed subtractive manufacturing. However, during the procedure, the deposits are subjected to rapid thermal stresses which adversely impact the integrity of the built component. High entropy alloys are materials with complex compositions of multiple elements. Traditionally, these alloys are fabricated using casting and other machining processes, with a recent interest in the use of laser deposition as a possible manufacturing process. To optimize process parameters of high entropy alloys melted on a steel plate, the influence of preheating temperature on the overall quality, microstructure and hardness behaviour of the alloys for aerospace applications were investigated. In this research, 9 samples of AlCoCrFeNiCu and AlTiCrFeCoNi high entropy alloys were fabricated using different laser parameters. The phases, chemical composition, micro-hardness and structural morphologies were characterized with XRD, EDS, Vickers Microhardness tester and SEM respectively before and after preheating the base plates at 400 °C. Experimental results show extensive cracking on all the samples without preheating while after preheating all samples were observed

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M. Dada (✉) · P. Popoola
Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa
e-mail: dadadupeola@gmail.com

P. Popoola
e-mail: PopoolaAPI@tut.ac.za

N. Mathe · S. Pityana · T. Lengopeng
Council for Scientific and Industrial Research, Pretoria, South Africa
e-mail: NMathe@csir.co.za

S. Pityana
e-mail: SPityana@csir.co.za

T. Lengopeng
e-mail: TLengopeng@csir.co.za

S. Adeosun
Metallurgical and Materials Engineering, University of Lagos, Akoka, Nigeria
e-mail: samsonoluropo@yahoo.com

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to be crack-free. Although, there were no variations on the dendritic structures in the optical micrographs with and without preheating temperature, there were notable changes in the phases and hardness behaviour of the alloys showing that preheating the base plate from 400 °C significantly influences the mechanical properties of additive manufactured high entropy alloys and contributes to the elimination of cracks induced by thermal stresses.

Keywords Base plate preheating · High entropy alloys · Laser additive manufacturing · Optimal parameters · Thermal stresses

Introduction

Manufacturing defects are flaws or irregularities in a component attributed to errors in production from surface quality issues, misalignments, dislocations, pores, aluminium oxides and residual stresses [1]. The laser additive technology which uses a laser beam contrary to other conventional methods is associated with minimal distortions after production ascribed by the control of heat contributed and energy supplied [2, 3]. The rate of melting and cooling are high, which results in solid solution phases and an excellent microstructure [4]. However, non-uniform strength existing in the heat-affected zone and the deposition bed is prone to develop internal stresses [5, 6]. These stresses depend on cooling rates, thermal expansion coefficients, phase transformations and the elastic behaviour of the material. The defect occurs when no external load after thermal treatments of the final component exists and this deteriorates the dimensional accuracy, corrosion and fatigue resistance [7]. Thus, generating a large strain, which results in cracks through the heat gradient from the deposits to the base plate [8]. Therefore, to minimize the high-temperature gradient, preheating of the base material is used. Zumofen and Beck [9] studied the impact of preheating temperature in selective laser melting (SLM) due to deformation and crack formation observed when fabricating carbon content steels and the authors suggested that heating the base material is a likely approach to reduce internal stresses and temperature gradients. Using the same technique, Malý and Höller [10] fabricated Ti6Al4V and Casati and Hamidi Nasab [11] fabricated AlSi10Mg Alloy with both authors recommending high preheating temperatures as a significant parameter. Danlos and Costil [12] proposed using pulsed laser irradiation to remove film contamination which had little effect on the substrate surface. However, preheating the substrate was distinguished to be important for better results. In a study to improve the property of stainless steels by surface treatments, Aghasibeig and Fredriksson [13] and Zhang and Shi [14] demonstrated how energy deposition method is the most proficient technique and preheating is a remedy to prevent cracks after deposition. Preheating drives moisture and contaminants reducing the rate at which the part cools down thus preventing locked-in stresses which can inhibit crack formation [15]. Cracking not only disconnect the coating from the mounting plates but also limits the optimization of the process parameters and its application. Materials processed using laser additive manufacturing technology must have good weldability, whilst avoiding cracks during rapid solidification and limited study has been done on preheating while using direct energy deposition technique in fabricating high entropy alloys(HEAs). In this study, the effect of preheating the plates as a solution to cracking during optimization of laser parameters on the microstructural and hardness properties of HEAs by laser deposition was investigated to understand the fundamental susceptibility of high entropy alloys to cracking and the methods of stress reduction.

Materials and Methods

Materials for the laser cladding process was prepared by mixing commercial 16.6w% Al, Co, Cr, Fe, Ni, Cu and 16.6w% Al, Ti, Cr, Fe, Co, Ni elemental powders with a purity higher than 99.6% purchased from F. J. Brodmann & CO., L.L.C. Tables 1 and 2 shows the chemical composition of the HEA powders as delivered by the manufacturer. Before cladding, sandblasting the surface of the base plate to be coated was achieved to minimize reflectivity to the laser radiation and improve the bonding strength between each alloy and the plate. Figure 1 shows the preheating furnace fixed at 400 °C, a temperature at the furnace's capability with the base plates in an electrically operated platform before the deposition procedure. The different compositions were fabricated with and without preheating by keeping the beam diameter, carrier gas and powder federate constant at 2 mm, 2 I/min and 2 g/min, respectively. While the laser power and scan speed were varied from 1200 to 1600 W at 8–12 mm/s for AlCoCrFeNiCu high entropy alloy [16] and AlTiCrFeCoNi HEA had a variation from 1400 to 1600 W at 8 and 12 mm/s with a 50% overlap. Figure 2 shows a continuous-wave ytterbium laser beam system (YLS) used to produce the alloys with a fitted robotic arm comprising both a nozzle and powder feeding system controlled by a computer-aided design (CAD) software system.

Tables 3 and 4, shows the laser parameters for this study. These were taken out from previous studies during the optimization process of parameters in terms of cladability of the HEAs and crack-free microstructures.

Table 1 Chemical composition of AlCoCrFeNiCu HEA in atomic percentage

Element	Al	Co	Cr	Fe	Ni	Cu
Amount	16.6	16.6	16.6	16.6	16.6	16.6

Table 2 Chemical composition of AlTiCrFeCoNi HEA in atomic percentage

Element	Al	Ti	Cr	Fe	Co	Ni
Amount	16.6	16.6	16.6	16.6	16.6	16.6

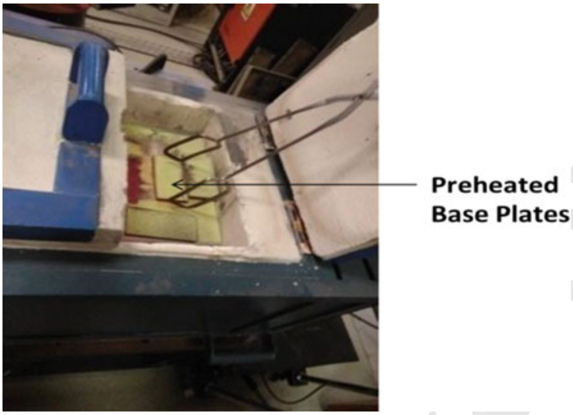

Fig. 1 Preheating furnace

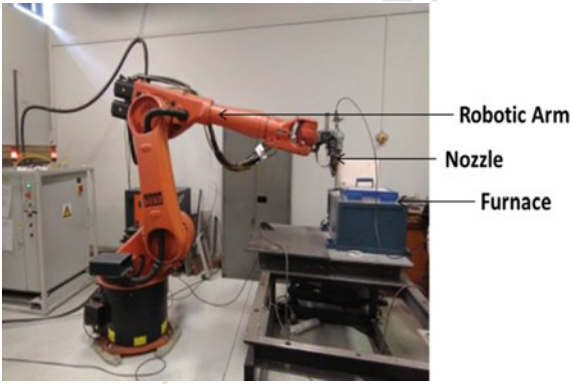

Fig. 2 Ytterbium laser deposition system (YLS)

Table 3 Laser parameters AlCoCrFeNiCu HEA

Baseplate preheating temperature (°C)	Laser power (W)	Powder feedrate (g/s)	Scan speed (mm/s)	Samples	Energy density (J/cm^2)
400	1200	2	8	A	7.5
400	1200	2	10	B	7.5
400	1400	2	12	C	8.75
400	1600	2	10	D	10
400	1600	2	12	E	10

Table 4 Laser parameters AlTiCrFeCoNi high entropy alloy

Baseplate preheating temperature (°C)	Laser power (W)	Powder feedrate (g/s)	Scan speed (mm/s)	Samples	Energy density (J/cm^2)
400	1400	2	8	F	8.75
400	1400	2	12	G	8.75
400	1600	2	8	H	10
400	1600	2	12	I	10

After cladding, all samples were sectioned into smaller pieces with Struers metallographic cut-off machine and the cross-sections of the sample were prepared using standard metallographic procedures namely mounting, grinding, polishing and etching with Kroll for the AlTiCrFeCoNi specimen and aqua regia solutions for the AlCoCrFeNiCu specimen. The transverse piece of the clads was examined using X-ray diffraction system (XRD), Optical microscope (OM), Vickers hardness tester, Scanning Electron microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS).

Results and Discussion

Effect of Preheating Temperature on Microstructure and Phase Structure

Figure 3 show X-ray diffraction patterns of the AlCoCrFeNiCu and AlTiCrFeCoNi HEAs, before and after preheating. Before preheating, the body-centred cubic (BCC) structure was observed attributed to the cocktail effect of Al and Cr with high bonding strength and melting point respectively in the BCC phase increasing the slip resistance and young modulus [17, 18]. After preheating, a minor $\{111\}$ reflection of FCC structure was formed near the $\{110\}$ plane as shown in Fig. 3b attributed to the concentration of Cu with an FCC structure promoting the formation of FCC solid solution [19]. The high Al content shows the larger atomic size effect of the aluminium atoms which expands both the BCC and FCC structures in accord with the report by Tong and Chen [20]. Al is known to have the FCC structure nonetheless; it is not known to contribute to the FCC solid solution phase formation. According to the phase fraction by Gibbs, the number of elements in an alloy and the equilibrium phases is given as $p = n + 1$. For a six element composition, where R is the gas constant at 8.314 J/mol K and n is the number of elements [21]. The mixing entropy $\Delta Smix = RIn(n) = RIn6 = 1.792R$, thus, this makes the formation of phases in both AlCoCrFeNiCu and AlTiCrFeCoNi HEAs a simple solution of FCC and BCC phases after preheating as seen in Fig. 3b–d. High entropy alloys with an increased

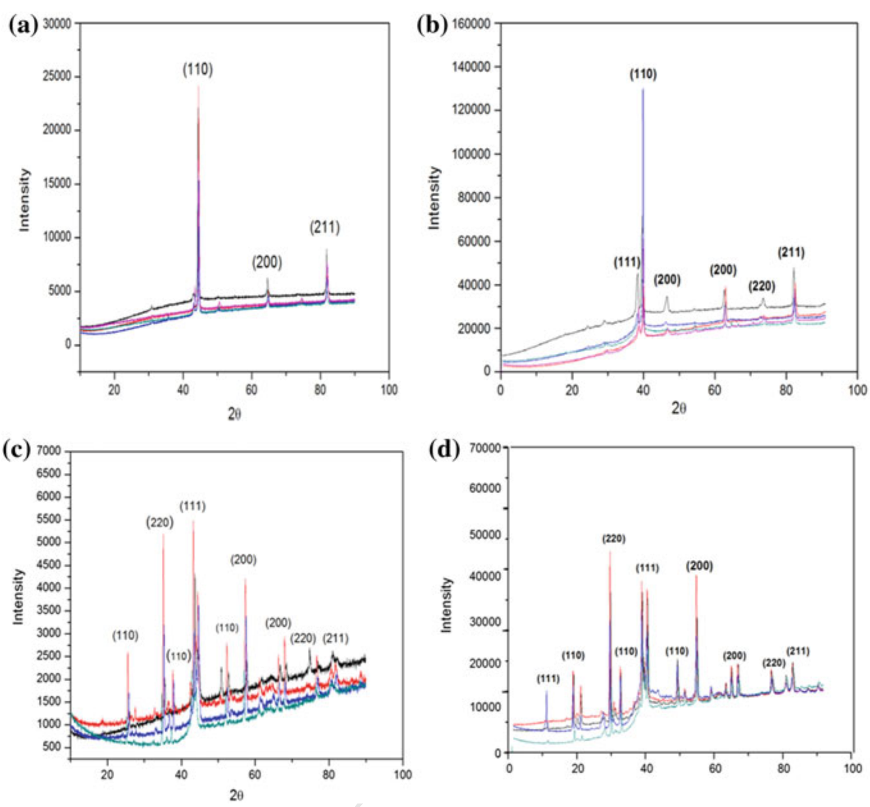

Fig. 3 XRD graph of AlTiCrFeCoNi and AlCoCrFeNiCu HEAs **a** AlCoCrFeNiCu HEA before preheating, **b** AlCoCrFeNiCu HEA after preheating, **c** AlTiCrFeCoNi HEA before preheating, **d** AlTiCrFeCoNi HEA after preheating

number of principal elements easily result in solid solutions enabling the alloy more stability at elevated temperatures especially for aerospace applications. The highest peak intensity {110} in AlCoCrFeNiCu HEA with preheating temperature was relatively stronger than without preheating temperature possibly indicating a preferential orientation of crystal growth contrary to the AlTiCrFeCoNi HEA were the highest peak intensity was lower after preheating as seen in Fig. 3c, d.

Figures 4 and 5 shows the optical micrograph of the clad cross-section of the HEAs coatings. From the results, there was micro-crack defects in the coatings without preheating conversely, after preheating temperature, there were no cracks observed. Noticeably, there was a homogeneous combination between the coating and the base plate. Results also confirm that the HEAs had fine dendritic characteristics attributed to the rapid heating and solidification of each progressive layer during deposition as shown in Fig. 6. The SEM images of both alloys are shown in Fig. 7 confirming the microstructures of both alloys comprising an equiaxed dendritic structure with the

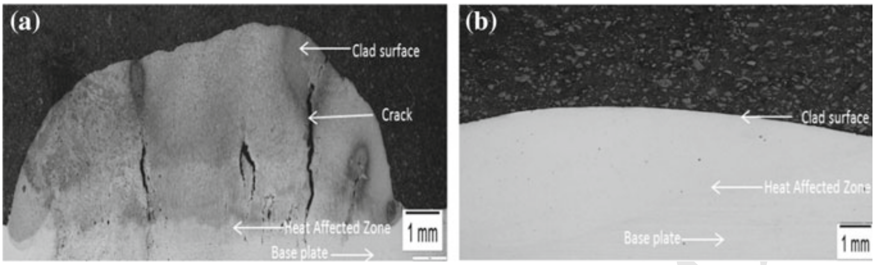

Fig. 4 Cross section of AlCoCrFeNiCu high entropy alloy **a** Before preheating temperature and **b** After preheating temperature

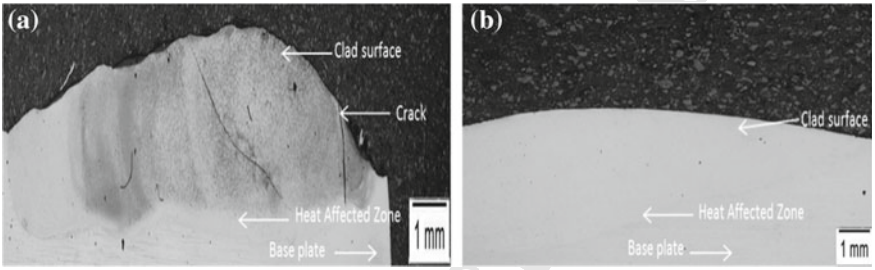

Fig. 5 Cross section of AlTiCrFeCoNi high entropy alloy **a** Before preheating temperature and **b** After preheating temperature

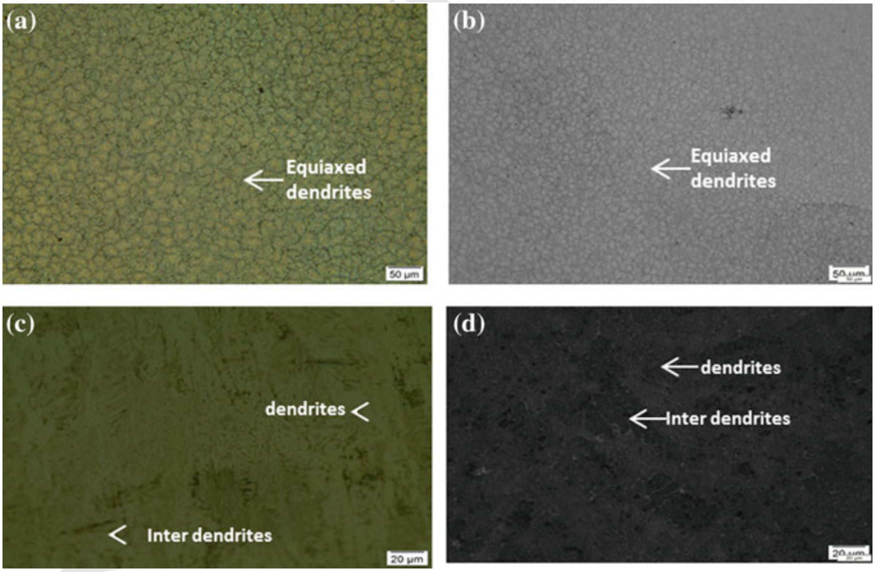

Fig. 6 Optical micrographs of AlCoCrFeNiCu and AlTiCrFeCoNi high entropy alloy **a** AlTiCrFeCoNi before preheating, **b** AlTiCrFeCoNi after preheating temperature, **c** AlCoCrFeNiCu before preheating, **d** AlCoCrFeNiCu after preheating

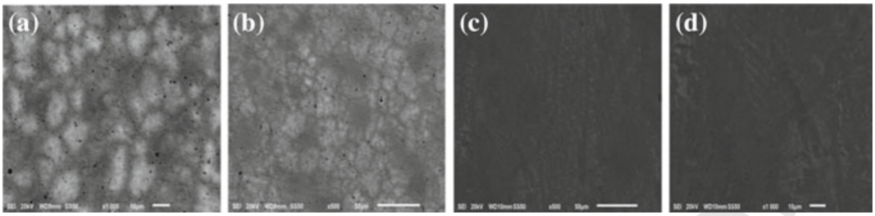

Fig. 7 SEM images of **a** AlTiCrFeCoNi before preheating, **b** AlTiCrFeCoNi after preheating temperature, **c** AlCoCrFeNiCu before preheating, **d** AlCoCrFeNiCu after preheating

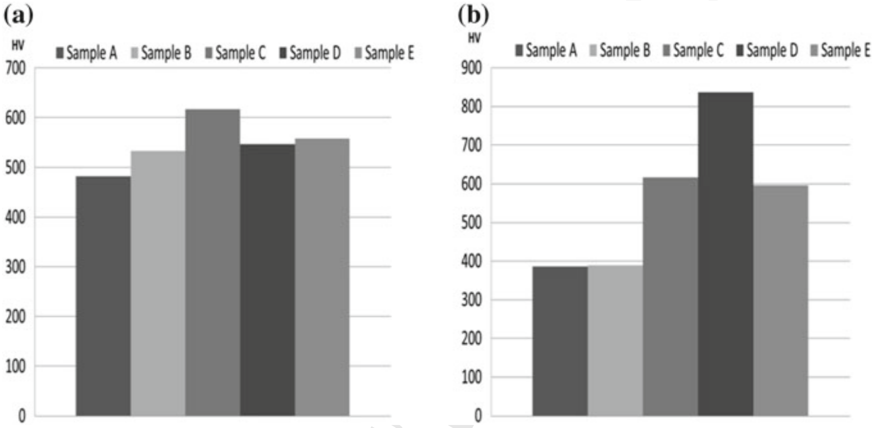

Fig. 8 Hardness chart of **a** AlCoCrFeNiCu before preheating, **b** AlCoCrFeNiCu after preheating

dendrites forming a grain structure in the AlTiCrFeCoNi HEA while the AlCoCrFeNiCu HEA had a typical dendrite and inter-dendrite structure with no significant changes occurring with and without preheat temperature. The segregation of Cu to the inter dendrite is expected as observed from the alloy composition from literature attributed to the low binding energy of Cu with other elements [19].

Effect of Preheating Temperature on Micro Hardness

Figures 8 and 9 shows the Vickers hardness charts of AlCoCrFeNiCu and AlTiCrFeCoNi HEAs under different process parameters with a single preheat temperature of 400 °C. As seen from the graph, sample A and B after preheating the baseplate experienced a 24% reduction at 7.5 J/cm^2 energy density each. Sample D and E experienced an increment after preheating with about 33% and 10% respectively at an energy of 10 J/cm^2 each while sample C maintained the range of the hardness of 600 HV at 8.75 J/cm^2. From the data, it can be deduced that the preheating temperature

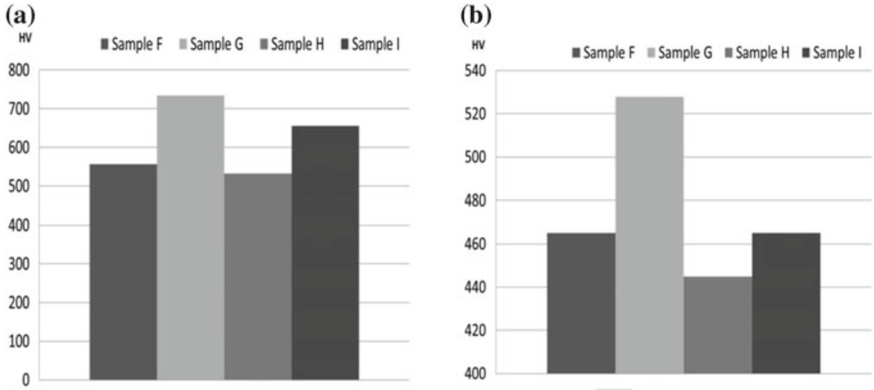

Fig. 9 Hardness chart of **a** AlTiCrFeCoNi before preheating, **b** AlTiCrFeCoNi after preheating

influenced the energy density of the alloys. Generally, with the preheat temperature, the AlCoCrFeNiCu HEA hardness goes up. Exhibiting an average hardness value of 450–600 HV before preheating, the values increases to the range of 350-800HV after preheating attributed to the predominant BCC phase and the reduced distance between the grains, thus, strengthening the grain boundary. The BCC structures are known to be more uneven and less dense, making the alloy possess increased lattice friction and reduced inter-planar spacing.

On the other hand, for the AlTiCrFeCoNi HEA, all samples after preheating experienced a reduction with the average hardness values reduced from the range of 380–800 HV to 400–500 HV attributed to the inner microstructure undergoing intricate phenomena during preheating under reoccurring thermal cycling resulting in the reduction in hardness values [22].

Conclusion

High entropy alloys deposited on steel base plate by direct energy deposition was studied. During optimization of process parameters, the HEAs were sensitive to cracking; therefore, the effect of preheating the base plate on the microstructure and hardness of the HEAs to eliminate residual stresses were examined using experimental analyses. The results proved that preheating the base plates at 400 °C is an effective way of eliminating cracks.

- Extensive cracks were observed in the microstructures of both AlCoCrFeNiCu and AlTiCrFeCoNi HEAs without preheating.
- The mechanical properties of AlCoCrFeNiCu and AlTiCrFeCoNi HEAs were compared before and after preheating. There were significant variations in the average hardness values of both alloys although the AlTiCrFeCoNi HEA had higher hardness before preheating. The AlCoCrFeNiCu HEA had an increment

from 450–600 HV before preheating to 350–800 HV after preheating showing that adequate preheat temperature can improve the mechanical properties of the alloy while the AlTiCrFeCoNi HEA experienced a reduction in average hardness values from 500–700 HV before preheating to 450–550 HV after preheating attributed to heat accumulation during preheating which reduces the cooling rate and temperature gradient thus forming a coarse dendritic columnar grain which lowers hardness values.

- Laser deposition with energy density between 8.75 and 10 J/cm^2 at 400 °C preheating temperature produced the best microstructure and hardness properties for the AlCoCrFeNiCu HEA with dendritic morphologies; BCC and FCC phases.
- Comparing samples with and without preheating the base plates, preheating the base plates preceding to laser deposition obviously had a positive influence in elevating the crack resistance of the HEAs making the material less susceptible to defects.

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