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Direct laser deposition cladding of $Al_xCoCrFeNi$ high entropy alloys on a high-temperature stainless steel

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ABSTRACT

$Al_xCoCrFeNi$ (x = 0.3, 0.6 and 0.85) high entropy alloy (HEA) claddings were produced by coaxial direct laser deposition (DLD) on a 253MA austenitic steel substrate using a mixture of blended elemental powders. The effect of key processing variables on the formation of HEA claddings and the compositional mixing between the deposited layer and the substrate was investigated through a three-level parametric study on laser power, laser scanning speed, laser beam size, powder feeding rate and hatch distance. Using selected parameters, HEA claddings mostly free of defects were successfully manufactured with very minimal dilution. With an increase in the Al mole fraction from 0.3 to 0.6 and 0.85, the HEA claddings displayed an evolution of crystal structure from FCC, to FCC + BCC and BCC, accompanied by an increase in microhardness. The increased Al content also resulted in reduced microstructural stability of the coatings and hence higher level of thermal softening upon isothermal treatment at 1000 °C.

1. Introduction

High entropy alloys (HEAs) are a relatively new class of alloy system comprising of 4–5 principle alloying elements at a concentration between 5 and 35 at.% [1–5]. Contrary to conventional phase rule prediction, many HEA compositions form simple solid solutions instead of brittle intermetallic compounds [3–6]. HEAs possess many attractive properties such as high strength [3–5], excellent wear [7], corrosion [8] and thermal softening resistance [9], thermally stable microstructure [10–12], low inter-diffusion [13], and high oxidation resistance [14–17]. Therefore, HEAs are gaining interest as protective coatings for engineering alloys in critical applications.

HEA coatings have been produced on a metal surface by various techniques including welding [18], physical vapour deposition [19], thermal spraying [20], and laser cladding [14,21–33]. Focussing on laser HEA cladding fabrication, the vast majority of prior studies have used a static powder bed technique [14,21–27,33]. Here a layer of pre-alloyed or mixed power is placed on the substrate surface and scanned by a laser beam, which melts the powder and partially melts the substrate to create an alloy cladding with a metallurgical bond to the substrate. Studies of this process include successful formation of various HEAs on steels [23–27,33], copper [28,29], aluminum [30], magnesium [31] and titanium alloy [14] substrates, where the cladding displayed improved wear and corrosion performances relative to the substrate. A clear practical limitation of this process is the ability to treat only flat and horizontal surfaces. In contrast, direct laser deposition (DLD) is a technique where the powder is inert gas transported and melted by a focused laser attached to a multi-axis head, and is routinely used to additively manufacture complex geometry metallic parts or to discrete area clad/repair of components [34]. Despite the clear advantages of this “blown powder” laser deposition technique its use in HEA cladding is rare [31,32].

Motivated to improve wear and corrosion resistance, Yue et al. [31] have reported an attempt to clad a magnesium substrate with an AlCoCrCuFeNi HEA by a direct blown powder cladding technique. The choice of substrate, with its boiling temperature below the HEA melting point, created difficulty and required a complex processing route. Also, severe intermixing between the substrate and deposit (i.e. dilution) occurred, wherein only the top 50 μm of a total coating thickness of 200–300 μm had an approximate HEA composition. One further study by Ocelík et al. [32] used a blown powder technique to fabricate AlCoCrFeNi and AlCrFeNiTa HEA claddings on an AISI 305 stainless steel plate. A blended mixture of elemental powders was used, which offers process convenience, however this resulted in some unmelted tantalum powder due to a very high melting point. Additionally, a strong dilution effect (mainly Fe from the substrate) was experienced which required three successive ~600 μm layer depositions to finally achieve the desired HEA composition in the outer layer. It is worth noting that both

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Table 1
Processing parameters and cladding metrics of I) single track deposition, II) square deposition trials on $Al_{0.3}CoCrFeNi$ and III) $Al_xCoCrFeNi$ coatings.

Trial number		Laser power P (W)	Scanning velocity S (mm/min)	Laser beam diameter D (mm)	Powder feed rate F (g/min)	Hatch distance H (mm)	Laser track width W (mm)	Build-up height T_C (μm)	Penetration depth T_P (μm)	Interface thickness T_D (μm)	Dilution F_D (%)	Powder efficiency P_E (%)	Energy density E_S ($J{\cdot}mm^{-2}$)
I	I-a. Pre-scan	800	800	3	/	/	1.36 ± 0.1	0	68	/	/	/	25.5
	I-b. Baseline	1000	800	3	F = ~13.6	/	1.9 ± 0.02	491 ± 32	110 ± 10	10.3 ± 1.6	12.5	30.1	31.8
	I-c	800	800	3	F	/	1.1 ± 0.11	261 ± 0.18	45 ± 0.8	7.75 ± 1.1	11.3	9.3	25.5
	I-d	1200	800	3	F	/	2.13 ± 0.03	554 ± 28	162 ± 0	13.75 ± 3.9	17.3	38.1	38.2
	I-e	1000	400	3	F	/	1.92 ± 0.01	639 ± 18	158 ± 12	22.5 ± 4.5	14.6	20.5	63.7
	I-f	1000	1200	3	F	/	1.17 ± 0.04	167 ± 16	54 ± 14	7.5 ± 1.4	19.5	9.1	21.2
	I-g	1000	800	2	F	/	1.86 ± 0.04	500 ± 34	194 ± 16	14.75 ± 2.1	21.6	30.2	47.8
	I-h	1000	800	4	F	/	0.8 ± 0.03	36 ± 4	59 ± 4	/	/	0.9	23.9
	I-i	1000	800	3	0.5F	/	1.74 ± 0.02	207 ± 24	119 ± 6	22.5 ± 1.4	29.9	22.4	31.8
	I-j	1000	800	3	1.5F	/	1.59 ± 0.04	550 ± 40	45 ± 5	7.3 ± 1.6	5.3	19.5	31.8
II	II-a	1000	800	3	F	0.75	/	932 ± 17	176 ± 7	24 ± 5.6	8.6	32.9	90.3[a]
	II-b	1000	800	3	F	1	/	816 ± 7	192 ± 8	21.5 ± 5.1	10.5	38.4	74.4[a]
	II-c	1000	800	3	F	1.5	/	604 ± 7	196 ± 7	20.5 ± 3.6	14	42.7	62.5[a]
III	$Al_xCoCrFeNi$	1000	800	2	F	1	/	845 ± 7	108 ± 3	30.9 ± 4.2	9.1	39.8	78.7[a]

[a] The energy density per unit of deposition volume ($E_V = P / (S{\cdot}T{\cdot}H)$, in $J{\cdot}mm^{-3}$) is used, where $T = T_C + T_P$.

these prior studies were performed by the side-cladding variant of blown powder DLD.

Here powder is delivered using a lateral/side powder feeder nozzle, which can cause variation in cladding characteristics (e.g. “against hill” or “over hill” cladding) depending on the relative motion of the laser head to the powder stream [34]. There have been no reported studies on HEA claddings by coaxial DLD, where the powder is delivered coaxially with the laser beam, and thus free from geometric constraints. Although there are notable first attempts at blown powder laser deposited HEA claddings, to advance the field there is a need for a systematic parametric approach and a detailed microstructural undertaking to address the critical issues encountered by this technology including dilution, compositional inhomogeneity, powder efficiency etc.

In the present study, the $Al_xCoCrFeNi$ (x = 0.3, 0.6 and 0.85) HEA system was chosen for coaxial DLD claddings from elemental powders on a 253MA high-temperature stainless steel substrate. It is well established in near-equilibrium cast HEAs that increasing Al content in this alloy system results in a transformation from face centred cubic (FCC) to body centred cubic (BCC) solid solution crystal structures [10,35]. In DLD processing, whether this HEA system holds its phase stability is of interest, considering possible dilution of HEA claddings and the rapid solidification rate (10^3–10^6 K/s), large thermal gradients (10^5–10^7 K/m) [36,37] and complex local thermal history between successive deposits during laser cladding. Herein, a systematic development path was taken including a 3-level 4-parameter study on single track deposits firstly performed to establish process conditions that optimise the deposit shape and minimise the dilution between coating and substrate. After that, multiple-track claddings were produced for all HEA compositions and extensively characterized for phase content, micro/macro-structure, crystallographic texture and chemical homogeneity. As a main target application of these coatings is to protect substrate alloys in high temperature oxidizing environments, the impact of thermal exposure (i.e. 1000°C for up to 100 h) on the deposit microstructure and properties (micro-hardness) was also examined.

2. Experimental procedure

In this study, the $Al_xCoCrFeNi$ (x = 0.3, 0.6 and 0.85 in atomic ratio) HEA coatings were produced by direct laser deposition on a 16 mm thick 253MA austenitic steel plate with an average grain size of ~40 μm in the hot-rolled and annealed condition. This steel has a composition of C0.03Cr24.0Ni14.3Si1.6Mn0.05 (wt%, Fe balance), which is specially designed mainly for high temperature applications up to 1150°C in oxidizing atmospheres [38]. The substrate plate was machined flat, sand blasted to reduce laser reflectivity and cleaned with acetone prior to deposition.

Direct laser deposition was performed using a TRUMPF TruLaser Cell 7040 coaxial blown powder laser deposition facility equipped with a twin powder feeder and a 1030 nm wavelength 4 kW TruDisk 4001 disc CO_2 laser. Herein, the $Al_xCoCrFeNi$ HEA claddings were fabricated from spherical gas-atomized Al, Co, Cr, Fe and Ni (~99.9–99.99% purity) powders in the size range of 50–150 μm provided by TLS, Germany and Micronmetals, USA. To avoid settling and segregation by density, the higher density element powders (Co, Cr, Fe and Ni) were firstly blended using a rotary tumbler for ~12 h. After that, the premixed CoCrFeNi powder and Al powder were loaded in separate hoppers and independently transported by a 99.999% ultra-high purity helium carrier gas to the focused laser on a 5-axis controllable head at carefully calibrated mass flow rates. The deposition region was sealed during cladding and continuously purged with high purity argon gas to maintain a relatively low oxygen atmosphere (< 20 ppm).

A single-track deposition parametric study of $Al_{0.3}CoCrFeNi$ was initially carried out to study the effect of key processing parameters on the deposit geometry and the extent of interface mixing. A pre-scan trial was first performed without powder flow rate to simulate a practical DLD operation with laser preheating of the substrate (Trial I.a, Table 1). This was followed by a matrix of experiments consisting of three levels of laser power (P), laser scanning speed (S), laser beam diameter (D) and powder mass feed rate (F) (Trials I.b–j, Table 1). After that, single layer squares (~20 × 20 mm) of $Al_{0.3}CoCrFeNi$ claddings were produced with varying hatch distance (H = 0.75, 1 and 1.5 mm, Trials II.a–c, Table 1) and the established parameters (Full trials III, Table 1) were applied to produce $Al_xCoCrFeNi$ (x = 0.3, 0.6 and 0.85) single layer claddings (hereafter referred to as $Al_{0.3}$, $Al_{0.6}$ and $Al_{0.85}$ HEA, respectively) with the dimensions of ~20 × 80 mm. All the depositions were produced at the focal working distance of 16 mm and by a building sequence of parallel vectors across the shorter dimension. $Al_xCoCrFeNi$ (x = 0.3, 0.6 and 0.85) claddings were polished flat by removing the top ~200 μm surface layer and then subjected to isothermal holding at 1000 °C for up to 100 h in air to assess the thermal stability of the HEA clad microstructures.

Phase determination was conducted on polished surfaces of the HEA claddings (~200 μm removed) using a laboratory PANalytical PRO MRD (XL) X-ray diffractometer with Cu Kα radiation in point focus. Microstructural characterization was performed on cladding cross-sections using optical microscopy (OM) and scanning electron microscopy (SEM), including backscattered electron (BED) imaging, electron backscattered diffraction (EBSD) and energy-dispersive X-ray spectroscopy (EDS). The samples for SEM, XRD analysis and hardness