Proceedings of the International Conference on Applied Mechanical Engineering Research (IC-AMER2019)
NIT Warangal, India – May 02-05, 2019
Paper No. XXX (The number assigned when the papaer is accepted)

Investigating High Temperature Oxidation of Hastelloy-X Fabricated by Laser assisted Directed Energy Deposition

K Dileep [a], A N Jinoop [b,c], C P Paul [b,c*], M Baral [b,d], Y Ravikumar [a], K S Bindra [b,c]

[a] *National Institute of Technology, Warangal-506004, Telangana, India.*

[b] *Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, Maharashtra, India.*

[c] *Laser Development and Industrial Applications Division, Raja Ramanna Centre for Advanced Technology, Indore-452013, Madhya Pradesh, India.*

[d] *Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore-452013, Madhya Pradesh, India.*

*Corresponding author Email: paulcp@rrcat.gov.in

Laser Additive Manufacturing using Directed Energy Deposition (LAM-DED) is an advanced manufacturing technique widely deployed for fabricating engineering components, repairing and large area cladding. LAM-DED is widely used for fabricating engineering components using various nickel super alloys such as Inconel, Hastelloy, Rene etc. Among the various superalloys, Hastelloy-X (Hast-X) is a Ni-Cr-Fe-Mo based high temperature creep, corrosion and oxidation resistant super alloy used for various high temperature engineering applications. In the present study, oxidation behaviour of LAM–DED built Hast-X is investigated at 850°C for short exposure period of 100 hrs. The oxidation behaviour is evaluated at different time intervals such as 6 hrs, 24 hrs, 50 hrs and 100 hrs. The oxidation behaviour shows approximately parabolic mass gain with time and oxide spallation is also observed during macroscopic analysis. A mass gain per unit surface area of 2.78146×10^{-3} Kg/m^2 is observed after 100 hrs of exposure. X-ray Diffraction confirms the presence of protective Cr_2O_3 oxide with less protective spinel $MnCr_2O_4$, $FeCr_2O_4$ and Fe_2O_3 along with matrix phase of Ni-Cr-Fe. The study paves way for further investigations on the microstructure and mechanical property of Hast-X after oxidation exposure.

***Keywords*:** Laser Additive Manufacturing, Directed Energy Deposition, Hastelloy-X, Oxidation

1. Introduction

Laser Additive Manufacturing (LAM), one of the Metal Additive Manufacturing (MAM) processes is widely deployed for fabricating three dimensional engineering components in layer by layer fashion directly from 3D CAD model data [1-3]. LAM technology is capable of fabricating "feature based designed and manufacturing" products and repairing existing prime components [1-4] with improved functionality. The technology has an edge in the fabrication of complex shaped engineering components, particularly of rare materials. LAM offers many advantages over conventional subtractive techniques such as ability to develop functionally graded parts, the reduction in production time and better process control [2]. LAM is successfully reported for various applications in automotive, aerospace, machinery, medical and power generation sectors [2]. LAM can be classified into Powder Bed Fusion (LAM-PBF) and Directed Energy Deposition (LAM-DED) based on material feeding. LAM-PBF uses lasers to selectively melt regions of a powder bed as per the geometry requirements, and LAM-DED melts a thin layer of injected material on the desired loci at the substrate surface or previously deposited material using numerical control code as per the solid model. A number of successive layers are deposited one over another resulting in three dimensional (3D) near net shaped components [2]. LAM-DED is successfully deployed for processing various Fe – based, Co-based and Ni-based alloys [5].

Aerospace, power generation, chemical and petrochemical industries are employing LAM to optimize buy and fly ratio by lowering production cost through reduced scrap in manufacturing, utilizing customised and complex component fabrication using LAM [4]. These

components are exposed to high temperature and corrosive environment leading to degradation of material and early failure of components. Thus, Nickel based super alloys are primary choice for such applications. Among the various Nickel based super alloys, Hastelloy- X (Hast-X) alloy is a Ni-Cr-Fe-Mo based alloy possessing excellent oxidation resistance, fabricability, high-temperature strength, stress corrosion cracking resistance, good ductility at elevated temperatures etc. Hast-X is a suitable material for fabricating components for ultra- super critical power plants (USCPP) and these components are subjected to high temperature oxidation. In Nickel based Super alloys, selective oxidation of Cr in Chromium oxide (Cr_2O_3) is observed at elevated temperature that form protective oxide and reduces further oxidation of alloy [6-7] leading to higher oxidation resistance.

LAM-DED is considered as a greener route for fabricating components like multi-material compact heat exchangers for USCPP applications. There is no previously reported work on the oxidation behaviour of LAM-DED built Hast-X. In one of our previous works, the process is developed for fabricating defect free Hast-X and the microstructure and mechanical properties are evaluated. It was observed that the yield strength, ultimate strength and micro-hardness is intermediate to that of cast Hast-X and LAM-PBF built Hast-X. Further, microstructural characterization revealed defect free fabrication with columnar dendrites in the build direction [8]. In the present work, an attempt is made to investigate the oxidation behaviour of LAM-DED built Hast-X and to study the effect of oxidation behaviour on the macroscopic features, mass gain and phase formation.

2. Materials and Methods

In the present work, an indigenously developed 2kW fibre laser based LAM-DED system is deployed for depositing Hast-X. The system consists of a 2 kW fiber laser, 5 axis manipulator in a glove box, computer numerical controller, coaxial nozzle, twin powder feeder, gas analysers and infra-red camera with image processing hardware. Further details of LAM-DED system is available somewhere else [1]. SS 304L substrate is used for depositing Hast-X. Laser beam spot diameter of 2.5 mm is deployed for depositing Hast-X. Argon flow rate of 6 litres/min is used for carrying Hast-X powder to the deposition zone. LAM-DED process parameters used for depositing Hast-X are: Laser power :1600 W, Scan Speed: 0.5 m/min and powder feed rate: 8g/min [8].

Gas atomized Hast-X powder with spherical morphology is deployed for LAM-DED. The composition of the Hast-X powders is as per ASM standard and is presented in our previous work [8]. The powder particle size in range of 45-105 µm is used for LAM-DED.

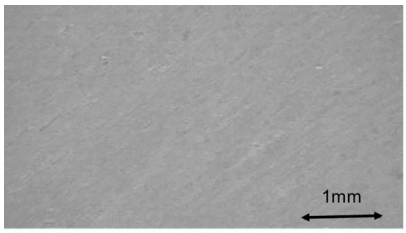
LAM-DED deposited Hast-X blocks are separated from the SS 304L substrate and samples are extracted using wire electric discharge machine (W-EDM). The extracted samples of size 30 x 20 x 2 mm^3 are grounded and polished with SiC polishing paper from 180 – 600 grit size. The EDM wire scars are removed and samples are prepared with same surface conditions confirming to ISO “ISO/TC 156 CD 21608” guidelines for high temperature oxidation test. Subsequently, samples are ultrasonically cleaned in water and further cleaned using acetone. The samples are dried before placing in the furnace. Mass of the dried samples is measured three times using electronic weighing machines with 0.1mg accuracy and average mass is recorded. Before placing samples, alumina crucibles are heated till there is no change in mass. A high temperature furnace with quenching facility (Make: Therelek) having a maximum operating temperature of 1400 °C is used for the investigation. Furnace temperature is raised to 850°C and samples are introduced to the furnace environment. Test is performed for 100 hours and samples are removed from the furnaces at definite intervals of 6 hrs (OX-6), 24 hrs (OX-24), 50 hrs (OX-50) and 100 hrs (OX-100). Macroscopic analysis of the oxidised samples is performed using a digital microscope. Subsequently, mass of the sample is measured after exposure for different time period. X-ray diffraction (XRD) study is carried out by using X-ray diffractometer (Make & model: BRUKER-

D8 Advance) from 20 – 100°. Cu Kα radiation (λ = 1.54 Å) at 40 kV and 40 mA is used in a continuous scan mode.

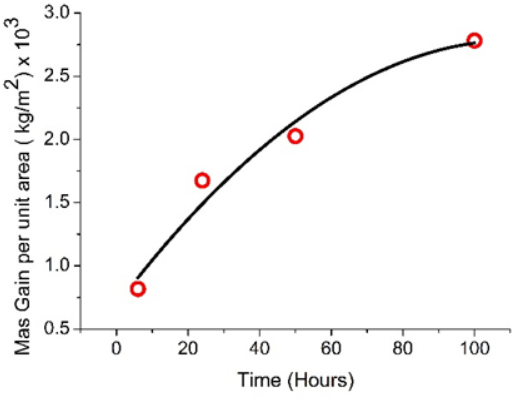
3. Results and Discussions

3.1 Macroscopic Analysis

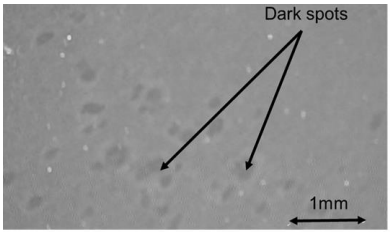
LAM-DED samples are analysed using a digital microscope after oxidation testing. The macroscopic examination of OX-6 samples revealed dark grey with greenish shades indicating the formation of Cr2O3. In Fig. 1(a) and 1(b) the scales are primarily well adhered with the sample surface along the sample surface while few dark spot areas presenting spall out of scale is also seen locally [8]. It is also observed that the samples kept for longer time especially OX-100 sample show grey and black strongly adhered oxide scale.



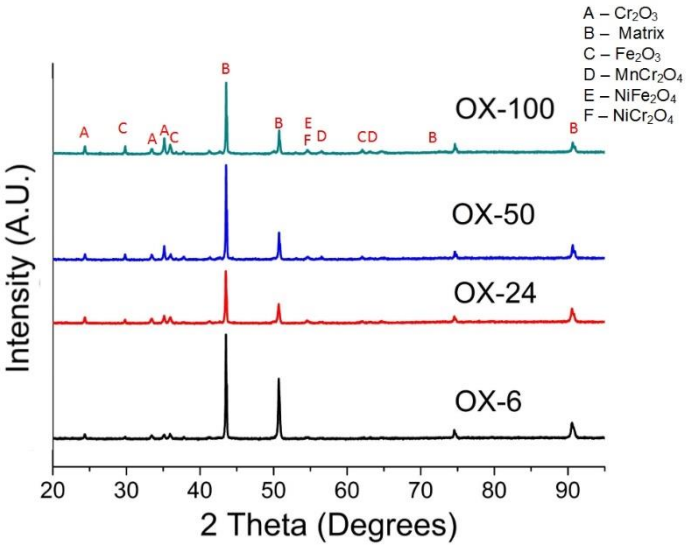
(a)



(c)



(b)



(d)

Fig. 1. Oxidation of LAM-DED built Hast-X a) Digital microscope images presenting well adhered scales b) Digital microscope images presenting spall out of scale c) Mass gain per unit area at different exposure time d) XRD plot at different exposure time

3.2 Mass Gain

The oxidised samples are subjected to mass measurement using a high precision electronic weighing balance with 0.1 mg accuracy. Fig. 1(c) presents mass gain per unit area (kg/m^2) with

exposure time. A rapid mass gain up to 24 hrs is observed which can be due to higher diffusion of oxygen due to the formation of initial thin layer of less protective oxides Fe and Ni scales. It is also observed that the rates of mass gain in OX-50 and OX-100 samples are less as compared to OX-24 mainly due to thick protective chromium oxide formation. Chromium possess selective oxidising property that forms strong and thick chromium oxide scale that reduces transportation and diffusion of oxygen ions through the scale and reduces rate of reaction that control further degradation of alloy [6]. It is seen that the mass gain during oxidation follow approximately parabolic behaviour with slight variation from parabolic mainly because of spallation of scale locally [8]. As per previous works by Rene Olivares et al., the kinetics of super alloys during oxidation follow the relation $(\Delta W)^n = Kt$, where K is isothermal constant, ΔW is mass gain per unit area, n is the rate exponent and t is time [9]. Considering regression fitting with parabolic curve approximate value of K is found 0.118×10^{-6} Kg^2/m^4hr presenting high oxidation resistance of LAM- DED manufactured Hastelloy-X. Further, the relation is extrapolated and percentage of mass gain is reduced to less than 2 % after 600 hours of exposure. Other examinations like long term oxidation and adhesion cohesion test of the oxides with the surface is being planned.

3.3 X-ray Diffraction

Fig. 1(d) presents the XRD data of LAM-DED fabricated Hast-X after oxidation for different exposure period. It confirms the presence of protective Cr_2O_3 peaks with matrix phase of Ni-Cr-Fe and Fe_2O_3 oxide at all the conditions.

Spinels of $MnCr_2O_4$, $NiFe_2O_4$, $NiCr_2O_4$ is observed after oxidation for all the conditions. The chemical reactions leading to the formation of Cr_2O_3, $NiFe_2O_4$, $NiCr_2O_4$ spinel and Fe_2O_3 are presented in equation 1-5 [9,10] due to isothermal oxidation as per Ellingham–Richardson diagram [6,11]

$2Cr(s) + 3/2O_2(g) = Cr_2O_3(s), \quad \Delta G_{Cr2O3} = -1092.44+0.238T$ (1)

$2Fe(s) + 3/2O_2(g) = Fe_2O_3(s), \quad \Delta G_{Fe2O3} = -815.02+0.251T$ (2)

$Ni(s) + 1/2O_2 = NiO(s), \quad \Delta G_{NiO} = -53.6+0.0084T$ (3)

$NiO(s) + Cr_2O_3(s) = NiCr_2O_4(s), \quad \Delta G_{NiCr2O4} = -53:6 + 0.0084T$ (4)

$NiO(s) + Fe_2O_3(s) = NiFe_2O_4(s), \quad \Delta G_{NiFe2O4} = - 19.9 - 0.0038T$ (5)

For OX-6 spinel $MnCr_2O_4$, $NiFe_2O_4$, $NiCr_2O_4$ shows peaks with lower intensity, while the intensity of these peaks increased with higher exposure due to higher diffusion of oxides of Mn, Fe and Ni to chromia scale after long time exposure.

Conclusion

Isothermal high temperature oxidation test in air environment of LAM-DED fabricated Hast-X is performed. Macroscopic studies, Mass gain measurement and XRD is used to analyse the oxidised samples. Mass gain measurement revealed approximately parabolic relation between mass gain per unit area and exposure time indicating rapid oxide formation during initial exposure period with slight reduction in the oxidation rate for 50 and 100 hours. Chromium oxide is the dominating oxide with the presence of spinel of Ni, Cr and Mn due to diffusion of these elements in chromia scale. Further studies on the composition variation, microstructure, mechanical properties after oxidation, adhesion cohesion tests are under investigation.

Acknowledgements

K Dileep and A N Jinoop acknowledges the financial support from Ministry of Human Resource Development, Govt of India and Department of Atomic Energy Govt of India, respectively. The authors acknowledge the support of Mr. H Kumar, Mr. U Kumar and Mr. C H Prem Singh for sample preparation. The authors thank the support of Dr. Archna Sagdeo and Ms. Preeti Pokhriyal for XRD testing. Authors thank technical support and fruitful discussion with Mr. S K Nayak, Mr. S Yadav, Mr. A Sahu, Ms. C. Nidhi and other members of LAM Laboratory at RRCAT during the course of the work.

References

[1] C. P. Paul, A. N. Jinoop and K. S. Bindra in: Rupinder Singh, Editor, Additive Manufacturing Application and innovation, Vol.1, CRC press, Boca Raton (2018).
[2] I. Gibson, D. Rosen, B. Stucker, Editors, Additive Manufacturing Technologies 3D Printing, Rapid Prototyping and Direct Digital Manufacturing, Vol. 2, Springer-Verlag New York (2015).
[3] G. K. Lewisa, E. Schlienger, Mater. Des. 21, 417 (2000).
[4] L. Bian, N. Shamsaei, and J. M. Usher, Editors, Laser-Based Additive Manufacturing of Metal Parts Modeling, Optimization, and Control of Mechanical Properties, Vol. 1, CRC press (2018).
[5] F. Caiazzo, Opt. Laser Technol.103, 193 (2018).
[6] D. J. Young, Editor, High temperature oxidation and corrosion of metals, Vol.2, Elsevier publishers (2016).
[7] N. Birks, G. H. Meier, F. S. Pettit, Editors, Introduction to the High-temperature oxidation of metals, Vol. 2, Cambridge University Press (2006).
[8] A.N. Jinoop, C.P. Paul, K.S. Bindra, Opt. Laser Technol. 109, 14 (2019).
[9] S. K. Rhee and A. R. Spencer,J. Electrochem. Soc. 119, 396 (1972).
[10] Q. Jia, D. Gu, Opt. Laser Technol. 62, 161, (2014).
[11] H.J.T. Ellingham, J. Soc. Chem. Ind. Banner 63 125 (1944).