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Solid State Additive Manufacturing of Oxide Dispersion Strengthened-FeCrAl Alloy Components for High-Temperature Supercritical CO2 Power Cycle Applications

April 2025

Saumyadeep Jana Amrita Lall Zachary C Kennedy Michelle D Fenn



Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory Richland, Washington 99354

Executive Summary

This project aims to demonstrate a sintering-based metal additive manufacturing as an alternative solution compared to laser powder bed fusion (L-PBF) method to fabricate HX components made of novel structural alloys. A unique sintering-based solid state additive manufacturing (SSAM) method has been used to fabricate novel shaped HX components made of high-strength FeCrAl alloy powders needed in high temperature supercritical CO2 (s-CO2) Brayton power cycle for intended use at a Gen-3 concentrated solar power (CSP) plant. Oxide dispersion strengthened (ODS)-FeCrAl alloy demonstrates a perfect combination of good mechanical strength and excellent corrosion resistance at elevated temperatures, and thus it can be an effective substitute for expensive Ni-base alloys (e.g., Inconel 625) currently used in Gen-3 CSP plants. However, melt-solidification based AM methods are unable to preserve the critical microstructural features needed in ODS-FeCrAl alloy for achieving high strength. SSAM method has the ability to preserve needed microstructural features in an ODS alloy. The proposed SSAM method works on the principle of material extrusion additive manufacturing (MEAM), and hence uses metal powder loaded filaments as printing feedstock. Specific objectives of this project include:

- 1. Fabricate high strength FeCrAl powder-loaded filament feedstock
- 2. Optimize MEAM printing parameters using custom-made FeCrAl filament
- 3. Design thermal treatment and sintering trials to achieve high degree of densification (>98%) in MEAM-printed 3-D parts.
- 4. Build novel-shaped HX component using FeCrAl filaments
- 5. Establish mechanical properties of MEAM-built FeCrAl components

Technical Achievements

In this research, material extrusion additive manufacturing (MEAM) has been explored as an SSAM method for fabrication of 3-D components using ODS-FeCrAl alloy. MEAM-printed 3-D parts go through a series of process steps, e.g., chemical treatment, thermal treatment etc. in order to create a high density fully metallic part. Final 3-D part quality is associated with various process steps, e.g., filament fabrication, print design, and thermal treatment optimization. In MEAM, a metal powder loaded filament is used for printing 3-D shapes. Composition of the filament is very important since it provides shape retention at low-to-medium temperature. There are a few commercially available metallic alloy filaments. However, FeCrAl alloy filaments are not commercially available. In this project, we came up with a method to fabricate high quality composite FeCrAl filaments that could be used for MEAM printing. Subsequently, we have optimized MEAM print methods to fabricate samples that are larger than 10 mm, by using a modular print design approach. Finally, we have been able to optimize the chemical and high temperature heat treatment steps to achieve very high density (>98%) in sintered MEAM-printed products. Microstructural examination and mechanical tests confirm that SSAM process is able to preserve the nanoscale oxides in our studied ODS-FeCrAl alloy.

Impact

The results obtained from this research will provide SETO and other DOE offices with information about SSAM as an alternative manufacturing method for novel structural alloys. ODS-FeCrAl alloy

has attractive set of properties. However, near net shape fabrication using ODS-FeCrAl is challenging since the manufacturing needs to preserve certain microstructural features. Use of MEAM has been shown as an effective method to preserve critical microstructural features in ODS alloys. Scaling up to component design and manufacturing is the next step, and we have shown some preliminary concepts in how that can be done. Further research with regards to ODS alloys, and SSAM method are recommended based on our current experimental results.

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1.0 Introduction

The US Department of Energy (DOE) Solar Energy Technologies Office (SETO) has been extensively investigating the supercritical CO2 (sCO2) power cycle since it has numerous features that is beneficial to Concentrating Solar Power (CSP) power plants. It is one of the technologies that can help meet the program's 2030 CSP levelized cost of electricity (LCOE) targets: 5 ¢/kWh for baseload power plants (with \geq 12 hours of thermal energy storage) and 10¢/kWh for peaker units (≤ 6 hours of thermal energy storage). The sCO2 power cycle outperforms the Rankine Cycle in efficiency for a given heat transfer fluid outlet temperature and can effectively use air cooling with minimal impact on performance. It features compact and easily manageable turbomachinery, making it simple to build, install, and operate. Additionally, it integrates well with high-temperature heat transfer media even at smaller scales and is scalable to 10-100 MW while preserving high efficiency, as outlined in a recent report [1]. A possible pathway to reach SETO CSP LCOE target for 2030, necessitates a power cycle efficiency of >50%, costing < \$900/kWe and dry cooling [1]. Analysis of sCO2 Brayton cycle reveals that a 50% cycle efficiency with dry cooling can be achieved with a turbine inlet temperature of approximately 715°C for recompression or partial cooling cycles. Improved sCO2 power cycle efficiency at a reasonable cost is a major research focus area for SETO regarding CSP technology. Requirements for high temperature (>700C) and high pressure (>20 MPa) to realize improved efficiency in a sCO2 power cycle has led SETO to focus on developing components capable of handling extreme pressures and temperatures [1].

In sCO2 systems, heat exchangers are a critical component in determining the overall efficiency, size, and performance of the system. In sCO2 systems, three types of heat exchangers are typically used: (i) the heater, which absorbs heat from the heat source; (ii) the recuperator, which transfers heat from the turbine exhaust to the compressor exhaust; and (iii) the cooler, which expels heat to the environment. In recent times, the SCO2 recompression Brayton cycle (RCBC) has been the most recognized cycle layout, as depicted in Fig. 1 [2]. Effectiveness of RCBC is closely linked with the performance of recuperators. As an example, it has been shown that the thermal efficiency of the cycle improves with higher total recuperator conductance. Additionally, the cost of the cycle is closely linked to the recuperators, with up to 90% of the cycle cost being attributed to heat exchangers. Therefore, strong incentive exists to develop high-performance recuperators at a low cost. The performance metrics of recuperators are defined by heat transfer and pressure drop. A desired recuperator for an sCO2 power cycle requires high heat transfer effectiveness (>90%); low relative pressure loss (<3%); good resistance to oxidation, corrosion, and creep at a high temperature (>650 °C); compact lightweight matrix at low cost; etc. [3].



Fig. 1 Super critical CO2 recompression Brayton cycle (RCBC) needs efficient recuperators [2]

Printed circuit heat exchangers (PCHEs) are currently the state-of-the-art recuperators for sCO2 systems due to their compact size, structural rigidity, and reliable performance under extreme pressure and temperature conditions. An example of a typical PCHE is shown in Fig. 2 [2]. Heat exchanger core in a PCHE consists of stacks of flat metal plates with fluid flow channels that are either chemically etched or pressed into the plates, and subsequently diffusion bonded. Despite their excellent heat transfer capabilities, PCHEs face significant challenges due to the non-linear channels, which result in substantial pressure drops because of longer flow paths and complex channel geometries. Since PCHE core connected the header becomes a single block, cleaning PCHEs is challenging. Therefore, PCHE performance can be significantly affected in a fouling environment. In addition, up to 90% of the cost of the sCO2 Brayton cycle could be tied to heat exchangers assuming the use of PCHEs, because of high manufacturing cost. In a recent report, the cost of PCHE recuperators intended for sCO2 application is noted to be 2,500 \$/(kW/K). Based on the available literature data, the cost of a PCHE recuperator for a 10Mwe SCO2 Brayton cycle is estimated to be \$ 2.4-3.2 M [4].



Fig. 2 Example of a PCHE (printed circuit heat exchanger), and the cutout drawing shows numerous micro channels present within [5].

Currently, material choice for construction of heat exchangers for use in s-CO2 system for operation at elevated pressures and temperatures, is limited by corrosion, oxidation and

creep resistance of the selected materials. Stainless steels such as 316L, 304, and 347 have been used since these are typically low-cost material. However, the highest operating temperature remains limited to 600-650C when stainless steels are used as the structural alloys for sCO2 heat exchangers (HX). Ni-base alloys such as Inconel 625 or Ti-alloys such as 22 Cr duplex can be an alternative material solution to achieve higher operating temperature (up to 750C), however at a much higher capital cost [5]. Therefore, there is a strong incentive in finding a solution for structural materials for SCO2 HX. Ideal structural material should show high temperature strength, and corrosion resistance while remaining cost-comparable to stainless steels. Oxide dispersion strengthened (ODS) alloys are known to show improved strength at elevated temperature. One potential ODS alloy for sCO2 application could be ODS-FeCrAl alloy, since it has good strength at elevated temperature, and shows exceptional corrosion resistance due to protective alumina surface film. However, it is critical maintain certain microstructural features in ODS alloys after part fabrication.

Additive Manufacturing (AM) or three-dimensional (3D) printing, is an advanced manufacturing method that can create intricate 3D parts with near-net shape directly. This process involves fabricating a 3D solid object straight from a digital CAD file. AM constructs products by layering and bonding successive sheets of material, where each layer holds the shape of a slice of the digital model. AM improves heat transfer in heat exchangers and heat sinks by allowing for the creation of intricate geometries and optimizing surface area more effectively than traditional methods. In addition, AM also allows for the creation of complex porous structures with predefined shapes and material options that can lead to improved heat transfer properties. Currently, selective laser melting (SLM), a laser powder bed fusion (L-PBF) AM method is being predominantly used for fabrication of advanced HX. HX made by SLM method using a Ni-based Haynes-282 alloy powder is reported to achieve a lowpressure drop with an effectiveness of 90% and a power density in excess of 10 MW/m3, for use in sCO2/molten salt heat transfer environment [6]. However, melt-solidification and repeated thermal cycling- based SLM method leads to challenges such as (i) achieving microstructural stability, (ii) formation of columnar grain structures and associated undesirable anisotropic properties, and (iii) high residual stress and related internal cracking. High infrastructure cost and energy intensive process are additional challenges for SLM as well.

This project aims to demonstrate a unique sintering-based solid state additive manufacturing (SSAM) method to fabricate novel shaped HX components as a lower-cost solution compared to currently practiced L-PBF methods. Specifically, material extrusion additive manufacturing (MEAM) has been investigated as an alternative AM method in this research. MEAM works by extruding filaments through a heated nozzle to build a freeform 3-D shape [7]. Composite filaments are made by mixing target metal powder and a blend of multi-constituent thermoplastic polymeric binders (sacrificial and backbone) that become soft and viscous (i.e., shear-thinning from a rheological perspective) when flowing through the heated nozzle. The multi-component polymeric binder act as an adhesive to keep the metallic powder particles together for shape retention during part printing/shaping process.

Subsequently, the 3-D built part goes through (i) a debinding operation to remove the polymeric binders, and (ii) densification through conventional pressure-less sintering at high temperature to fuse metallic powder particles together. This unique shaping debinding sintering (SDS) AM method offers several advantages compared to more popular metal AM methods that include: (i) low cost of AM equipment, (ii) ability to work with a very small amount of powder, (iii) ability to create an equiaxed microstructure and related isotropic properties, (iv) maintain composition homogeneity, and (v) almost zero residual stress in the built parts. A schematic of the MEAM method is shown in Fig. 3. We have developed MEAM method for ODS-FeCrAl alloy, since we believe MEAM can be an effective AM method in preserving the key microstructural features present in ODS-FeCrAl alloy for it retain high strength and corrosion resistance at elevated temperature, which is critical for sCO2 applications.



Fig. 3 Schematic of material extrusion additive manufacturing (MEAM) method – one of the SSAM methods available, showing major process steps (i) filament fabrication, (ii) 3-D part printing, and (iii) densification through binder removal process and sintering.

2.0 SSAM process development and qualification on coupon level samples

This project has done technical evaluation of filament extrusion-based MEAM technique, a type of available SSAM method. Major process steps for filament extrusion-based MEAM method are the following:

- 1. Composite filament fabrication
- 2. 3-D part print parameter development
- 3. 3-D part densification through debinding and sintering

2.1 Composite FeCrAl filament fabrication

Success of MEAM process depends on the quality of metal powder loaded composite filaments. A good quality filament requires good mechanical strength for shape retention, buckling resistance and flexibility, which depends on physical attributes (size, shape, volume fraction) of the FeCrAl powder and the nature of polymeric binders added. For successful fabrication of a high quality composite FeCrAl filament, we investigated the following parameters:

(i) polymeric binder chemistry, (ii) compounding parameters, and (iii) metal powder loading in the composite filament.

1. <u>Selection of polymeric binder chemistry</u>:

For the fabrication of polymer-bound FeCrAl filament, the multi-constituent polymeric binder plays an important role toward fabrication of 3-D shape through SSAM method. The **backbone polymeric binders** provide structural strength to the 3-D part and helps in shape retention at elevated temperature until the onset of sintering of metallic powders. The **sacrificial binders** are used to induce flowability during filament extrusion for easy part printing. **Additives** are included to achieve better homogenization of the polymeric blend and create uniform distribution of metal powders in the fabricated filament. Details about the polymeric binder components that have been considered and/or screened are summarized in Table 1. Detailed screening and down selection of the polymeric binder during processing with high volume fractions of FeCrAl included as well as their solubility and thermal decomposition behaviors for solvent extraction and thermal debinding methods, respectively.

Optimization	Sacrificial binder	Main/Backbone binder	Additives
parameters			
Volume	paraffin wax, synthetic PP wax,	OBC, PP, Irogran A85 P	Stearic acid
fraction	Lanco 1394 LF, SEBS G401.A55B	4350 TPU, LDPE, HDPE	

Table 1: List of polymeric binders screened

2. Filament compounding:

A co-rotating twin screw micro-compounder was used for making the filaments on the bench scale (~12 mL volumes) that allows for efficient screening of new formulations while mimicking the processing conditions on pilot scale or larger compounders. Temperature and screw speed are the typical process parameters that are varied to fabricate a good filament. Fig. 4 shows the micro-compounder and images of some of the representative FeCrAl filaments that were fabricated during this project. A comprehensive summary of our FeCrAl filament development work is presented in Table 2, which details the binder chemistry, FeCrAl metal content, and some of the compounding parameters. We were able to increase the FeCrAl powder content up to 65% by volume (~94% by weight) in one of our fabricated filaments (AM100_14).



Fig. 4 (a) micro-compounder equipment, (b) spooled FeCrAl filament, 56% FeCrAl content by volume, (c) fabricated filament extruded through a 400 μ m nozzle to check for printability, finer spooled filament in the center confirms good printability.

Filamen t ID	FeCrAl content , vol.%	Mass	Main binder	Vol. %	Sacrificial binder	Vol .%	Additive	Vol .%	Compoundin g temp, °C	Filamen t dia, mm	Max. Torque, N-m
AM100_ 1	56.0	92.0	OBC	33.0	paraffin wax	11	х		170	1.45- 1.5 mm	6 Nm
AM100_ 2	56.0	92.0	OBC	22.0	paraffin wax	22	х		100	1.7 mm	5 Nm
AM100_ 3	56.0	92.0	OBC	11.0	paraffin wax	33	x		85-105C		
AM100_ 5	56.0	92.0	PP	33.0	paraffin wax	11	x		140C	1.85 mm	
AM100_ 6	56.0	92.0	PP	33.0	synthetic PP wax	11	х		150C	1.7 mm	
AM100_ 7	56.1	91.0	PP	43.9	-	-	x		140C		20
AM100_ 8	59.0	91.9	PP	30.8	Lanco 1394 LF	10. 3	х		150		14.4
AM 100_9	56.0	89.5	lrogra n A85 P 4350 TPU	30.8 0	Lanco 1394 LF	13. 1	x		185		4.5
AM 100_10	56.0	91.0	polypr opylen e	33.0	SEBS G401.A55 B	11	x		165		17
AM 100_11	59.0	91.9	PP	30.8	paraffin wax	10. 3	x		150		8.6
AM 100_12	62.0	92.8	PP	28.5	paraffin wax	9.5	x		150		9.9
AM 100_13	62.0	92.9	PP	27.0	paraffin wax	9	Stearic acid	2	150		6.6
AM 100_14	65.0	93.7	РР	25.0	paraffin wax	8.3	Stearic acid	1.7	150		10.7

Table 2. FeCrAl filament fabrication study, summary of binder chemistry optimization during trial-I

3. FeCrAl metal powder loading:

For fabrication of composite FeCrAl filaments, the final binder formulation chemistry has been the use of PP (poly-propylene), PW (paraffin wax), and SA (stearic acid) based on our experience with printing and subsequent sintering behavior of the printed samples, and it appears that the filaments made with PP-PW-SA combination performs the best. Table 3 summarizes filament fabrication effort during trial-II. There is a critical limit to the maximum amount of PP that can be incorporated in a composite filament, and it seems 25% by vol. is a workable solution. Vol. % of FeCrAl powder was fixed at 65% while using two different powder size distributions, e.g. (i) 3:1 ratio of coarse to fine powder, and (ii) 100% fine powder. One attempt was made to make a filament (23 16) with higher powder loading of 70% by volume using 3:1 powder size ratio as well. 3 spools of 23_14 and 3 spools 23_15 filaments were made, each containing ~57 g of FeCrAl powder. Compounding and extrusion temperature varied between 130-145C during filament fabrication, and the surface quality of the fabricated filaments were smooth and could be easily spooled with a diameter between 1.5-1.7 mm. Overall, it appears 23 15 filament was easier to fabricate than 23 14. Fabrication of 23_16 was more difficult, indicating challenges in increasing FeCrAl powder loading during filament fabrication.

Increasing the vol. % of FeCrAl powder in composite filament, and use of multi-modal powder size distribution are supposed to have a beneficial effect on final densification after high temperature sintering, as is seen in conventional powder metallurgy processing. However, since SSAM needs a filament that can be smoothly extruded during both filament fabrication as well as 3-D shape printing process, there are additional requirements of having a filament with enough rigidity that can support shear force during the extrusion process, which means a certain vol.% of polymeric binder will be needed since the composite filament is essentially a polymer matrix composite.

Filomont ID	Polymeric binder				
Filament ID	PP	PW	SA		
SETO 23_14	25	8.3	1.7	65 (75% coarse, 25% fine)	
SETO 23_15	25	8.3	1.7	65 (100% fine)	
SETO 23_16	21.3	7.1	1.5	70 (75% coarse, 25% fine)	

Cross-section images of 3 filaments are captured in Fig. 5. Filaments SETO 23_14 and SETO 23_15 show a homogenous distribution of metal powder in the filament cross-section whereas the SETO 23_16 sample had large voids in the center of the cross-section. This points towards too high of metal loading and a low binder amount. Increase in metal powder loading, therefore, needs some more optimization.





TGA analysis

Characterization of FeCrAl filaments has been carried out to learn about the thermal stability and distribution of FeCrAl powder within the filament. TGA analysis provides the thermal decomposition behavior of polymer-bound FeCrAl filament. A representative TGA plot for filament # AM100_14 is shown in Fig. 6a. Two separate filament pieces were run in the TGA to get an idea about homogeneity of FeCrAl powder mixed with the polymeric binder, and also to confirm the vol.% of metal loading in the fabricated filaments. TGA analysis indicates FeCrAl powder loading to be >65%, which converted in mass fraction would be ~94%. This result demonstrates that polymer-bound filaments with very high metal loading can be fabricated for its use in SSAM method. In addition, successful fabrication of

such high metal loaded filament means that high density and minimal porosity should be expected in SSAM-built components during the densification step happening at the high-temperature sintering.

TGA analysis of composite FeCrAl filament made of FeCrAl powder, PP, paraffin wax, and stearic acid shows mass loss at two temperatures, i.e., ~200°C and 400°C. These temperatures correspond to the temperature where the sacrificial and backbone binder is lost through thermal decomposition. Binder decomposition temperature is a critical piece of information that is used for optimization of thermal debinding process. Fig. 6b and 6c represents micro-CT images of FeCrAl filament in transverse and longitudinal orientation. Uniform distribution of FeCrAl powder particles together with good mixing between the polymer blend and the powder particles within the fabricated filament is apparent from these two images. In addition, the filaments appear to be dense, and no large voids are observed, indicating overall success of the compounding process.





Metal loading in composite filament plays a critical role in determining final density of the sintered products in SSAM printed samples. We have attained >98% density when FeCrAl powder loading is 65% by volume in the composite filaments. We, therefore, attempted to increase FeCrAl loading to even higher value to attain better densification after sintering. It appears that a very high metal loading of 70% is not attainable. It makes the filament very brittle. The highest metal loading by vol.% is 66.5 in one of our composite FeCrAl filaments, without affecting its handling performance. For the rest of this project, we have worked with 65% by vol. FeCrAl filament.

2.2 3-D part print parameter development using composite FeCrAl filament

In MEAM, 3-D parts are fabricated by extrusion of the composite filaments that is pushed through a heated print nozzle. Target 3-D part is first sliced using a print software that converts the 3-D model into .stl file. Subsequently, the part is printed by optimizing a number of parameters. Following section provides a detailed description of MEAM printing parameter optimization study.

1. Print parameter development using small samples (5 x 5 x 3 mm)

Initial MEAM print parameter development was done by printing rectangular prisms with a targeted dimension of 5x5x3 mm. These cuboids were used for developing the binder removal and high temperature densification sintering steps. Following printing parameters were optimized to increase the quality of the printed parts in green state:

- Print speed
- Print nozzle temperature
- Extrusion feed rate
- Print layer height
- Extrusion multiplier

Optimization of these parameters were performed on a custom-built printer with a 300 mm x 300 mm x 270 mm print volume, an E3D V6 hotend and a BondTech extruder. Parts were printed onto a print bed with a PEI surface that was heated between 70-80 °C. Repetier Host was used to connect to and control the printer, and PrusaSlic3r and Slic3r were used to slice the parts. Print speed for this material was best between 15-20 mm/s, which is similar to off-the-shelf metal filaments. These improvements were visually detectable in the surface quality and smoothness of the parts, compared to when the material was printed at faster speeds. Tested nozzle temperatures ranged from 185 °C to 210 °C, with highest densification in the green state part occurring at 190 °C nozzle temperature. Table 4 report various printing conditions that were tried in using composite FeCrAl filament to fabricate 5x5x3 mm cuboids.

Cross-sectional images of the printed coupons in the green state are captured in Figure 7ai. printed cuboids showed presence of voids that are regularly spaced for samples A-F. Overall, the print conditions were sub-optimal for Sample A – Sample F. In our second trial, extrusion multiplier and the nozzle temperature were changed, and the smallest layer height of 0.1 mm was selected. Optimization of above-mentioned print conditions led to much denser cuboids in the green state (Figure 7g - 7i).

Densification of MEAM-printed samples after high temperature sintering is a technical challenge. Since MEAM method uses high weight % of polymeric binder (~ 7 wt.% has been used in this research), it leads to challenges during binder burn out. However, MEAM printing parameters can be optimized to overcome binder burn out challenge. It was noted that when

5x5x3 mm cuboids are printed using repeated open spaces, sintered density is significantly higher in comparison to a dense green print after sintering (Fig. 8).

Batch	Layer	Extrusion	Nozzle	Bed	Speed
	Height	Multiplier (%)	Temperature	Temperature	(mm/s)
	(mm)		(°C)	(°C)	
1_A	0.2	100	185	75	20
1_B	0.2	100	185	75	20
1_C	0.2	120	185	75	20
1_D	0.1	100	185	75	20
1_E	0.1	120	185	75	20
1_F	0.05	100	185	75	20
2_A	0.1	150	190	75	20
2_B	0.1	150	200	75	20
2_C	0.1	150	210	75	20

Table 4. Print parameters for 5x5x3 mm cuboid fabrication



Figure 7. Low magnification stereo microscope images of 5x5x3 mm cuboids; (a) Sample A, (b) Sample B, (c) Sample C, (d) Sample D, (e) Sample E, (f) Sample F, (g) Sample extruded at 190 °C, (h) Sample extruded at 200 °C, (i) Sample extruded at 210 °C



Fig. 8 MEAM green prints with regularly spaced open channels show higher density after sintering compared to a dense green print, which shows internal cracking.

2. Print parameter optimization study for 25 x 7 x 2 mm samples

Based on initial print parameter optimization study, next printing parameter optimization study was conducted for relatively larger samples. From earlier prints and observations, print settings of layer height and infill percentage were chosen for optimization due to their potential for impacting the overall densification of the part. Layer heights of 0.15 mm and 0.3 mm were selected with the hypothesis that fewer layers in a part (i.e. a thicker layer height) could potentially minimize the number of interlayer boundary conditions. In previous prints, voids have appeared to concentrate at these interlayer boundaries, and reducing the number of those could potentially decrease the overall porosity of the part. Thinner layer heights of 0.1mm and 0.05mm were tested in previous trials and were determined to be too thin to print consistently with high quality.

Infill percentages were also varied in this experiment to incorporate and quantify the effect of intentional voids in the green-state part. In previous sintering trials, it was observed that small channels in the green-state part provided better part densification than a denser and macroscopic void-free green-state part. Infill percentages of 100%, 95%, and 90% were chosen for the optimization study.

These parameters were explored for two filaments (SETO23_14 and SETO23_15, 65% FeCrAl loading by vol.) and were tested for two different sintering procedures. Each unique

condition was produced in triplicate, resulting in 72 printed samples (36 for each filament) as outlined in Table 5 below.

72	24 Conditions Printed in Triplicate
24	Individual Conditions
2	Filaments (SETO23_14, SETO23_15)
2	Sintering Trials (Vacuum, Hydrogen)
3	Infill Percentages (100%, 95%, 90%)
2	Layer heights (0.15mm, 0.3mm)
# Of Variables	Variable Details

Table 5.	Print r	parameter	optimization	studv
	· · · · · · · · ·		• p	

All printed components were in the form of a 25mm x 7mm x 2mm brick oriented in the X, Y, and Z directions, respectively. In addition to the varying parameters of layer height and infill percentage, each component was printed without perimeters (infill only). From previous trials, perimeters were believed to block gases released during the sintering process from escaping the part, resulting in trapped gas bubbles inside the part and large voids. All parts were printed with an alternating 45-degree infill pattern. When printed with 0.3mm layer height, each brick had 7 layers, and with a 0.15mm layer height, each brick had 13 layers. With the varying infill percentages, bricks required approximately 5mm more of filament for each 5% increase in infill.

For printing the coupons, nozzle was set to 185C, bed to 60C, and the speed was the same as previously used for other prints (<20mm/s). In addition to printing with SETO 23_14 and 23_15, an attempt was made to print using SETO 23_16 filament, which had the highest FeCrAl content by vol. %. SETO 23_16 was soft and brittle and had a slightly rough surface finish. We attempted to extrude the filament out of a 0.4mm nozzle set to 180 C, but initially had difficulty of the filament edges getting caught on the Teflon tubing that helps guide the filament into the heat sink and heat block, and resulted in grinding down of the filament at the extruder. Extruder set up was cleared and extrusion was attempted again at 185 C, material was able to be extruded through the nozzle. When a print was attempted however, the backpressure from the print was enough for the extruder to grind down the filament again, resulting in a failed print very early on. Therefore, it seems that the current formulation of 70% FeCrAl loading did not give us a workable filament. More work is needed to increase FeCrAl vol.% to 70 in a composite FeCrAl filament for successful SSAM printing.

Macroscopic images of printed coupons in green state are shown in Table 6 and 7, showing success using SETO 23_14 and SETO 23_15 filaments for printing coupon samples. It appears that use of a shorter layer height, i.e. 0.15 mm instead of 0.3 mm, leads to significant lateral spreading of two adjoining layers, which maynot be desirable. A major difference between 0.3 mm layer height vs. 0.15 mm layer height is the distance between two successive hollow regions. In the case of 0.15 mm layer, the distance is larger, while 03

mm layer height shows a more uniform netowork of hollow spaces. In the SSAM process, polymeric binders that are used to make the composite filaments are removed by a binder burnout treatment during thermal debinding step. During themal debind, polymeric binders form various volatile hydrocarbon gaseous phase. Having a network of uniformly spaced pores would help in better removal of volatile hydrocarbon species. Thus, 0.3 mm layer print condition should provide better opportunity for binder removal during thermal debind, which is critical towards achieving high density after sintering (Fig. 9).

SETO	23_14	0.15 mm layer height	0.3 mm layer height
Green mo	ntage		
90% infill			
			TANK IN CONTRACTOR OF THE OWNER OF THE
95% infill			
100% infil	1		CHURCHUR CHURCHUR CHURCH
100/01111	•	LING ALL LINE HERBERS	

 Table 6 SSAM printed sample cross-section stereo microscope image (green state)

Table 7 SSAM printed sample cross-section stereo microscope image (green state)

SETO	23_15	0.15 mm layer height	0.3 mm layer height
Green mo	ntage		
90% infill			Manakakanonalaisika
95% infill			
100% infill	l		



Fig. 9 Periodic open spaces within MEAM-printed 3-D shape optimized to achieve very high density after sintering.

3. MEAM printing capability study

MEAM print capability evaluation has been carried out by printing several bench-marking test pieces, as recommended in ASTM 52902. Bench-marking test pieces printed by MEAM method includes the following:

- 1. Resolution Pin (w/ 1 perimeter) part printed with 5 tallest columns, with one of the tallest columns being a hollow cylinder.
- 2. Resolution Pin (no perimeter) part printed with 5 tallest columns, with one of the tallest columns being a hollow cylinder.
- 3. Resolution Pin (square) (no perimeter) Part printed with 5 tallest columns, (with the second tallest having rounded corners, right next to the tallest rounded corners appear no different than square corners with no perimeters (visually)
- 4. Resolution Pin (square) (w/ 1 perimeter) Part printed with 5 tallest columns, (with the second tallest having rounded corners, right next to the tallest.
- 5. Resolution Hole (w/ 1 perimeter)
- 6. Resolution Hole (no perimeters)
- 7. Resolution Hole (Square) (no perimeters)
- 8. Resolution Hole (square) (w/ 1 perimeter)

Representative images of bench-marking test piece are shown in Fig. 10. These benchmarking test pieces after printing has been sintered. It appears that MEAM process is robust enough for printing larger sized features, but lacks printing resolution for fabrication of fine features.



Fig. 10 Resolution pin bench-marking test piece printed by MEAM. ASTM 52902 followed as a reference.

4. Printer Comparison between MakerBot and Rhombus Printers

We looked into the effect of MEAM printer on print quality. Different 3D printers can produce slightly different parts, even when sliced using the same settings. We observed a consistent signature of the 3D printer we have used up to this point in the project (a custom built Rhombus printer, Fig. 11a). We observed that the dimensional tolerances on this printer were slightly high which reflected in the production of the pieces by inconsistently printing the edges of the part. To decrease potential voids in the printed parts, we experimented with another 3D printer, a modified MakerBot Replicator 2 printer (Fig. 11b) with off-the-shelf hardware but a modified controller board to allow for open-source slicing and control.





Printer Details

The Rhombus Printer is a custom built high-temperature 3D printer. It is framed with V-slot linear rails and driven by belts for the X and Y axis and by dual threaded rods for the Z-axis. The heated bed is covered with a BuildTak printing surface sheet and topped with a PEI sheet and purple Elmers glue where the FeCrAl material is printed. The extruding system is comprised of a BondTech extruder and E3D hotend assembly with a steel heater block. The controller board is an Azteeg X3 Pro board with custom programmed Repetier-Host firmware.

The modified MakerBot Replicator printer remains similar to the off-the-shelf option with respect to hardware, with a few exceptions. Printer motion is controlled through belt driven X- and Y- axis and the Z-axis moves via a single threaded rod. The heated build surface is black anodized 356F aluminum and is covered with purple Elmers glue stick to get the part to adhere to the bed. The extruder system has been modified from the off-the-shelf construction to a BondTech extruder and an E3D hotend assembly with a steel heater block. The original controller board has been removed and replaced with an Azteeg X3 Pro board with custom programmed Repetier-Host firmware.

Test samples were printed on each printer and compared. We sliced a cube at three separate infills (90%, 95%, and 100%) with otherwise the same settings, and saved three separate g-codes that were then used on both printers. We printed the three cubes on each printer separately and then compared the print quality (Fig. 12).



Fig. 12 Printability test for two different printing platforms. (a) and (b) custom built Rhombus printer; (c) and (d) MakerBot Replicator 2 printer. Two sets of print parameters are used

After imaging the parts, we determined that the modified MakerBot Replicator printer appeared to print higher quality components, and we transitioned to printing with the modified MakerBot printer for the remainder of the prints. The test samples were printed at 0.3 mm layer height out of a 0.4 mm steel nozzle heated to 185 degrees C. The part was printed with a 0/90 raster angle. This was an additional change to previous prints, which we have previously printed at a 45/45 raster angle. We observed in earlier prints that printing at a 45/45 raster angle resulted in less ideal slicing patterns that could potentially result in higher voids. When sliced with the 0/90 raster pattern, the parts had clean corners and tighter lines in the slicer and this increase in quality was reflected in the print. This choice was maintained for all other prints printed this quarter. The only modification needed between the two printers is in their heated bed temperatures. The custom-built Rhombus printer could be set at 60C bed temperature and have the FeCrAl material adhere well to the bed. The printed material did not stick to the modified MakerBot printer with a bed temperature of 60C, but when the bed temperature was increased to 80C, the part adhered. This modification was also used for all subsequent prints.

2.3 **3-D part densification through debinding and sintering**

3-D printed part in green state contains FeCrAl powder mixed with a blend of polymeric binders. In order to get a fully metallic 3-D part, the polymeric binders need to be removed, which is done by debinding process. Final densification takes place through sintering at a high temperature.

Binder systems have been designed primarily to be removed by a combination of a solvent extraction step followed by a thermal decomposition process of the remaining backbone

polymer binder prior to FeCrAl particle sintering. Optimized composite FeCrAl filament have binder compositions consisting of polypropylene (PP), paraffin wax (PW), and stearic acid (SA). The PP main binder was designed to be removed by thermal degradation on the heating step prior to the sintering and densification of the FeCrAl part. PW and SA both are soluble in a variety of organic solvents and were designed to be removed in the solvent soak step.

Solvent debind

Cyclohexane at room temperature was shown to be effective for selective removal of the PW and SA components in the FeCrAl composites without disturbing the 3D-macrostructure of the composites. Composite filament pieces were submerged in cyclohexane for at least 16 hours. The solution was removed, the filament pieces were rinsed twice with fresh cyclohexane, and left to air dry for at least 4 hours. TGA analysis before and after the solvent extraction step was used to quantify FeCrAl loadings in the composites and verify the selective removal of the PW and SA components. The TGA data of as extruded filament made using batch-I FeCrAl powder is provided in Figure 13a. The initial mass losses in the TGA traces upon heating are from the PW and SA components where the bulk of the material is removed prior to 300 °C. The remaining mass loss step occurring from 300-500 °C is from the PP component. The remaining content is FeCrAl powder and the FeCrAl vol.% was calculated from the residual masses at 500 °C. TGA data recorded on the filament pieces after the cyclohexane soak (Figure 13b) determined that little to no mass was lost in all the composites prior to 300°C. This verifies the PW and SA components were successfully removed. The PP main binder thermal degradation step is the only mass loss step occurring. The estimated FeCrAl loadings in the composites have increased to as high as 73% on a volume basis because of the solvent debinding step. Fig. 13c shows the TGA plot for composite FeCrAl filaments made using batch-II FeCrAl powder. The mass loss behavior of FeCrAl filaments using batch-I and batch-II FeCrAl powder is noted to be the same. Therefore, soaking in cyclohexane appears to be an effective binder removal step for PW and SA components.

Subsequently, the effect of soak temperature in cyclohexane was studied. Same asfabricated FeCrAl filaments were submerged in cyclohexane at 21 °C and 42 °C for different durations of time, respectively. It was noted that dissolution of sacrificial binders (PW and SA) took place at a faster pace at 42 °C. In addition, soak at 42 °C lead to greater mass loss, indicating solvent debind is more efficient at above the ambient temperature. Details of the various solvent debind conditions are captured in Table 8. As can be seen, condition 3 with 16 hours of immersion in cyclohexane at 42 °C result in maximum removal of sacrificial binders.



Figure. 13. TGA data comparing mass of FeCrAl filaments before and after solvent debind steps ; (a) FeCrAl filaments, batch-I before solvent debind, (b) FeCrAl filaments, batch-I after solvent debind, (c) FeCrAl filament, batch-II

	Time (hrs)	Temperature (°C)	Average Mass Change (%)
Cond 1	16	21	-1.98
Cond 2	46	21	-1.98
Cond 3	16	42	-2.28

Thermal debind

Thermal debinding or the process of removing backbone binders by heating the sample is a complicated process. The binders need to be completely and gently removed without damaging the printed part before further heating the part for sintering at high temperature for final densification. Figure 14 shows the importance of thermally debinding with correct parameters. Transverse cross-sectional view of a composite FeCrAl filament in as-fabricated, after solvent debound condition are shown in Figure 14a and 14b, respectively. Figure 14c shows formation of large porosities in the cross-section of the solvent-debound filament heated to 960C and held for 1 hour. This is because as the sample was heated

through the backbone binder's boiling point, the backbone polymeric binder (PP) escaped by breaking the material apart.



Figure 14 (1a) Micro-CT image of transverse section of as-extruded coarse FeCrAl powder filament, (b) micro-CT image of transverse section of same filament in solvent debound state, (c) micro-CT image of transverse section of the same filament after solvent debound and heated to 960 C and held for 1 hr

Therefore, temperature, time, ramp rate and environment are very critical for thermal debinding this step. The temperature required depends on both the backbone binder thermal decomposition behavior and the ramp rate. Through TGA analysis, it was found that isothermal hold at 400 °C for 2 h was able to completely remove the PP-based binder for sample weighing ~70 mg heated at a ramp rate of 5 °C/min as seen in Figure 15a. In comparison only about half the binder was removed by applying an isothermal hold of 2 hours at 380 °C and as the temperature increases further, there is sudden mass loss as seen in Figure 15. TGA plot for FeCrAl filament made using batch-II powder is shown in Figure 15b. It further confirms that an isothermal hold at 400°C for 2 h is able to completely remove the backbone PP binder.



Figure 15 TGA plot demonstrates effective thermal debinding conditions, (a) comparison between 380C and 400C, (b) thermal debinding behavior of FeCrAl filament made using batch-II powder

Based on the TGA study, 400 °C has been selected as the thermal debinding temperature. The required hold time depends on the size of the sample. Thermal debinding trials were

conducted with 2, 8 and 12 h of hold time, with process details listed in Table 9. Since the backbone binder escapes through gasification at 400 °C hold, one of the major challenges in this step is to control printed layer delamination, since there is no physical bonds present between individual FeCrAl powders.

Low magnification images of the cuboids subjected to various thermal debind conditions are summarized in Figure 16. It was found that least damage to the printed layer and delamination were observed with 12-hour hold and a slow heating rate. Environment during thermal debinding plays an important role as well. Thermal debinding in air leads to possible absorption of oxygen and nitrogen, which can hinder sintering for alloys that are prone to oxidation. Therefore, thermal debinding cannot be conducted in air environment. On the other hand, vacuum environment creates a negative pressure and as the binder comes out of the part, adjoining layers delaminate and voids are created. Therefore, inert atmosphere works best for this step.

Temp	Ramp rate	Environment	Time	Comments
380C	5C/min	vacuum	2 hr	Abrupt binder removal damaging the layers
400C	5C/min	air	2 hr	Oxidation issues during sintering
400C	5C/min	vacuum	2 hr	Abrupt binder removal causing delamination
400C	5C/min	Ar	2 hr	Abrupt binder removal damaging the layers
400C	5C/min	Ar-H2	8 hr	Abrupt binder removal causing delamination
400C	1C/min	vacuum	12hr	Slight damage in layers
400C	1C/min	vacuum	12 hr	Gentle removal of binder

T 0 0		and the second second	1111
Table 9 Summar	y of thermal	debinding	conditions



Figure 16 Optical images showing the effects of various thermal debinding conditions

3.0 Sintering behavior of SSAM-printed FeCrAl Pellets

High-temperature sintering

Fabrication of a well-densified 3-D part made with composite FeCrAl alloy filament through MEAM finally depends on the success of high temperature sintering step. High temperature sintering process for FeCrAl alloy has been optimized by following steps: (i) understand critical sintering conditions for FeCrAl powder without any binders added, and (ii) design sintering heat treatment for MEAM-printed FeCrAl coupons, with optimized filament binder and MEAM print parameters.

1. FeCrAl alloy powder characterization

Kanthal is the world leader in producing various grades of FeCrAl alloys. Kanthal has generously provided us with their research grade FeCrAl alloy powder intended for additive manufacturing applications Characterization of as-received powders has been carried out to learn the following:

- 1. Powder size distribution
- 2. Powder morphology, size, and shape
- 3. Phase analysis
- 4. Chemical composition



Figure 17. Feedstock FeCrAl AM-100 powder (a) batch I (b) batch II

Table 10	. Powder	size d	istribution	details,	batch	l and batch II,	laser	diffraction	and S	SEM i	maging
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Characterization method	D10 (µm)	D50 (µm)	D90 (µm)
Laser Diffraction – Batch-I (by vol)	20.7±2.5	42.7±6.5	87.8±4.3
Laser Diffraction – Batch-II (by vol)	5.1	11.0	25.5



Figure 18 Particle size distribution plots for batch-I and batch-II AM 100 powder

Representative SEM images of the as-received FeCrAl powders are shown in Fig. 17. The particles are mostly spherical with smooth surface texture which are desirable traits for subsequent formulation and sintering steps. In addition, as shown in Fig. 17a, a bi-modal distribution of particles was noticed for batch-I. SEM image of the longitudinal section of a pressed pellet made of batch-II FeCrAl powder is shown in Fig. 17b. Distinct size difference between batch-I and batch-II powders can be easily observed. To get a detailed idea about the powder size, we carried out image-based powder size analysis of the as-received AM100 powder feedstock. Laser diffraction-based powder size analysis was also carried out. The details of powder size in terms of D_{10} , D_{50} and D_{90} values are provided in Table I, where D_x denotes the threshold size below which X% of the total powder population exists. Both the techniques show that the FeCrAl AM100 particle size is larger than those commonly used in sintering-based powder metallurgy routes for batch-I. However, the particle size for batch-II is noted to be significantly smaller. A comparison of the particle size using SEM images and laser diffraction method is provided in Table 10 and Fig. 18.

X-ray diffraction analysis on the feedstock powder has also been carried out, and the diffractogram is shown in Fig. 19. Based on the XRD data, the feedstock FeCrAl powder is noted to have a body centered cubic (bcc) structure, and therefore is a ferritic class of stainless-steel alloy. Spectroscopic analysis of FeCrAl feedstock powder was carried out using inductively coupled plasma-mass spectroscopy (ICP-MS) to understand the chemical composition, and the results are shown in Table 11. The chemical analysis indicates the presence of high wt.% of Al (~4.5%) in the feedstock. Carbon LECO test was performed on batch-II feedstock FeCrAl powder. It was found that the average (of three samples) carbon content in batch-II AM100 powder is 322.7 ppm or 0.032% by wt. O, N, H and C analysis of batch-I powder was also performed on the powders and determined a very similar carbon content (~ 0.03 wt.%)

Sample	ΑΙ	Cr	Со	Fe	Mn	Si	Ti	V	Zn	Zr
Sample 1	4.33	20.60	0.02	68.32	0.15	0.12	0.07	0.03	0.10	0.08
Sample 2	4.41	20.82	0.02	69.01	0.15	0.08	0.08	0.03	0.10	0.09
Average	4.37	20.71	0.02	68.67	0.15	0.10	0.07	0.03	0.10	0.09
Kanthal datasheet	4.5-5.5	19-23.5		Bal	0-0.4	07				

Table 11a. Chemical composition of the batch-I AM100 powder, wt.%

Table 11b. Leco analysis, wt.%

SAMPLE	0	Ν	Н	С
Batch-I	0.024%	0.099%	0.001%	0.026%
Batch-II				0.032%
Kanthal Datasheet				0.08%





Sintering of pure FeCrAl powder

We studied various aspects of sintering process in order to get an idea about right sintering condition for FeCrAl powder. Typical process route for FeCrAl alloy is the following: production of FeCrAl powder by atomization method, and subsequent hot consolidation and hot working method to fabricate various wrought forms. Information about pressure-less sintering route for FeCrAl is generally lacking. Sintering process optimization has been done by studying the effect of (i) sintering atmosphere, (ii) sintering temperature, and (iii) sintering time.

Sintering behavior of coarse FeCrAl powder (D₅₀ ~ 40 µm)

To understand the sinterability and to approximately find the conditions best suited for densification, we started with sintering experiments of pressed pellets made with coarse FeCrAl powder. This batch of powder was very difficult to press into a pellet as seen Figure 20a because of its large particle size. Figure 20b shows a pressed pellet made with batch-I FeCrAl powder that was heated at 1000C for 4 hours. The sample shows little to no neck formation.



Figure 20 (a) Pressed pellet made with first batch of FeCrAl powder and (b) optical image of the pellet after heating at 1000 C for 4 hrs in air

Effect of continuous heating up to 1380 °C in air vs argon

Sintering trials were carried out through dilatometer tests using pressed powder pellets in air and argon with a flow rate of 200 sccm by heating up to 1380 °C. Both the samples were observed under optical and scanning electron microscope (SEM) to understand the extent of densification and the remaining void fraction. The images of pellet heated in air shows a layer of Al-oxide forming on the surface of the FeCrAl particles and aluminium nitride crystal within the FeCrAl particles, confirmed by EDS mapping presented in Figure 21a-c. On the contrary, the pellet heated in argon, where the atmosphere control was not good enough, presented in Figure 21d-f shows a thinner layer of oxide on the surface particles and no Aluminum particles within the particles. This oxide layer prevents neck formation and thus impedes densification. This result demonstrates the need for sintering in an atmosphere with strict oxygen control for FeCrAl powder feedstock.



Figure 21 (a and d) higher magnification SEM image of FeCrAl sample sintered in air and Argon by heating up to 1380C; EDS elemental map; (b and e) Al-map, (c and f) Oxygen map

Sintering behavior of fine FeCrAl powder ($D_{50} \sim 11 \mu m$)

This batch of powder could be easily pressed into pellets compared to the coarse FeCrAl powder as seen in Figure 22a. It also performed better during sintering experiment. After heating at 1000 °C for 4 hours in Ar environments (Figure 22b) widespread neck formation is noticed.



Figure 22 a) Pressed pellets made from fine FeCrAl powder b) Sample sintered by heating up to 1000C for 4 hrs in Argon

Multiple sintering experiments were conducted at various temperatures between 700 °C to 1350 °C to find the optimal temperature for sintering where maximum densification occurs without any phase change or microstructural damage. As can be seen in optical images with a magnification of 50X in Figure 23, the decrease in porosity starts at temperature as low as 700 °C where neck formation was observed. This is indicative of the diffusivity and sinterability of FeCrAl alloy. At 1250 °C, the spherical particles can no longer be seen. Porosities reduce in size and are of cylindrical shape, which is a feature of intermediate stage of sintering. As the temperature was further increased to 1350 and 1380 °C, the porosity reduced and were of spherical shape which exhibits achievement of final stage of

sintering. Table 12 shows the void area fraction achieved by using different sintering conditions. It shows that higher temperature helps with better densification. Further optimizations are required to meet over 98% densification and were performed on the printed pellet.



Figure 23. Optical images of magnification 50X in a) as pressed pellet and after sintering b) at 700C for 4hr in Ar c) 1000C for 12hr in Ar d) 1250C for 2.5 hr in Ar e) 400C for 8h + 800C for 4hr +1300C for 4hr in Argon and f) 1380C 5hr in Ar

Sintering Conditions	Void Area Fraction
As is pressed pellet	36.301
700C 4hr Ar	14.1725
800C 4hr Ar	13.7025
900C 4hr Ar	14.082
1000C 4hr Ar	13.59
1000C 12 hr Ar	14.33
1100C 12 hr Ar	13.258
400C 8h + 800C 4hr +1300C 4hr Ar	6.17
1380C 5hr Ar-2.7%H ₂	5.574

Table 12. Void Area Fraction for different sintering conditions in pressed fine FeCrAl powder pellet

Next, sintering experiments were conducted on solvent debound MEAM-printed pellets. As pointed out earlier in this report, MEAM printing optimization study was started by making small 5x5x3 mm shapes. Those small prints were used for sintering optimization study. the major difference between MEAM-printed shapes and pressed FeCrAl pellet is the presence of multi-component binders in the former. Some of these binders (sacrificial and additives) are removed by solvent debinding process. However, the backbone binders are needed in MEAM printed 3-D shapes, as it provides structural support to otherwise loose FeCrAl powders for shape retention. However, the backbone binders get removed during thermal debinding treatment (400 - 600°C) from the MEAM printed 3-D shape. It is critical that FeCrAl

powders should start to show some degree of sintering initiation event (e.g. neck formation) in order to retain the printed shape.

Based on the results from sintering of pressed pellets, the sintering temperature was varied between 1000 °C and 1380 °C and the resulting void area fraction is summarized in Table 13, with details of sintering conditions tried. First signs of neck formation were observed in the sample sintered at 1250 °C for 2.5 hours. In the sample sintered at 1300 °C for 4 hours in reducing atmosphere, spherical particles can no longer be seen. Porosity size reduces and shape changes to cylindrical or spherical. As the sintering temperature is increased to 1325 °C, the porosity size decreases, and void area fraction falls to under 1% but there were some gaps between adjoining printed layer. At sintering temperature of 1350 °C, all the layers fuse together with a void area fraction of 2.9-4.0% depending on the print parameters. A summary of low-magnification overview of SSAM-printed cuboids after high temperature sintering is shown in Figure 24. Figure 25 captures 50X micrographs of various sintered samples, to give a closer overview.

Overall, it appears that use of vacuum during high temperature sintering leads to better densification for MEAM-printed FeCrAl pellets. It is possible that a vacuum environment at high temperature promotes better binder burn out, by forcing the various gaseous products that form during binder decomposition within the MEAM-printed shapes. However, use of vacuum during thermal debinding step (400 - 600°C) is not recommended, as it will result in very fast gas evolution, and damage the prints internally, based on our experience. Therefore, based on our experience the best sintering practice for MEAM-printed FeCrAl coupons should be the following:

Use of slow heating rate and long isothermal holds at appropriate thermal debinding temperature, followed by slow heating to high temperature and do long isothermal hold under vacuum to promote good densification of FeCrAl powders.

Temperature and Hold	Ramp rate	Environment	Print	Void Area Fraction	Comment
380C 2hr 1000C 12 hr	5C/min	Ar	Cylindrical	32.11	No sintering
400C 2hr 800C 2hr 1000C 4hr	5C/min	vacuum	Cylindrical	35.60	No sintering
400C 2hr 800C 2hr 1250C 2.5hr	5C/min	Ar	Cylindrical	22.82	Neck formation
400C 2hr 800C 4hr air +1100C 24h	5C/min	Ar	Cylindrical		Oxidation
400C 8h 800C 4h 1300C 4hr	5C/min	Ar-2.7%H ₂	Cylindrical	7.24	Intermediate sintering stage
400C 12h 1325C 24h	1C/min upto 700 then 3C/min	Ar	Cylindrical	0.98	Final Stage of sintering
400C 12h 1350 C 24h	1C/min upto 700 then 3C/min	Vacuum	Sample C	2.28	Final stage of sintering
400C 12h 1350C 24h	1C/min upto 700 then 3C/min	Ar	190C	4.24	Print related layer damage
400C 12h 1350C 24h	1C/min till 700C then 3C/min cool down 3c/min	Ar	Sample A, B, C, D, E, F, 190C, 200C, 210C, 190 asprinted, coarse 10x10x10		Oxidation
1380C 5 h	2c/min upto 1200C then .5C/min cool down 3c/min		air thermal debound 190C		Oxidation due to thermal debinding in air
1380C 5 h DIL/APEL	2c/min upto 1200C then .5C/min cool down 3c/min		air thermal debound Sample C		Oxidation due to thermal debinding in air
400C 12h 1380 12h in Argon purge vacuum	1c/min upto 700C 5C/min upto 1300C 1C/min upto 1380C		solvent debound B	2.91	Final stage of sintering

Table 13 Det	tails of sintering	conditions tried	on SSAM-printe	d FaCrAl nallats
	taits of sintening	contaitions theu	UII 33AM-printe	u recial pellels



400C 2h 800C 2h 1250C 2.5 hr Ar



400C 12h 1350C 24 hr vacuum



400C 8h 800C 4h 1300C 4hr Ar-H2



500 μm

400C 12h 1380C 12 hr vacuum

Figure 24. Low-magnification overview of SSAM-printed cuboids after high-temperature sintering



Figure 25. Sintered optical micrographs of SSAM-printed FeCrAl pellets. a) 400C 2hr +800C 2hr +1250C 2.5hr Ar b) 400 C 8h 800C 4h 1300C 4hr Ar-H2 c) 400C 12h 1325C 24h vacuum d) 400C 12h 1350 C 24h vacuum e)400C 12h 1350 C 24h vacuum f) 400C 12h 1380 12h vacuum

Pressure-less sintering condition optimization for larger MEAM-printed coupons

MEAM-printed rectangular blanks made using 65% vol. FeCrAl powder composite filament (SETO 23_14 and SETO 23_15) after solvent debound in cyclohexane, were sent out to a commercial MIM facility for thermal debind and high temperature sintering. 100% FeCrAl powder pressed pellets were also included as a control. Degree of densification in sintered samples has been measured by a variety of techniques e.g. (i) Archimedes method, (ii) optical imaging, and (iii) X-ray micro-CT.

MEAM-printed samples were sintered using two methods, (i) under vacuum, and (ii) under flowing H2. The details of sintering conditions are captured in Table 14. Various sintering trials in Hydrogen furnace conducted at PNNL and a commercial sintering facility showed improved in densification of pressed pellets as the temperature increased from 1250C to 1300C to 1325C to 1350C with further scope of improvement in densification. Therefore, for the next set of trials, a temperature of 1360C and an isothermal hold of 6 hours was selected.

RUN	THERMAL DEBIND TEMP 1 (C)	DEBIND HOLD 1	THERMAL DEBIND TEMP 2 (C)	DEBIND HOLD 2	TEMP C	TIME	ENVIRONMENT
1	450	3 hr	600	3 hr	1360	6 hr	vacuum
2	450	3 hr	600	3 hr	1360	6 hr	Hydrogen
3			400	12 hr	1300	1.5 hr	Hydrogen

Fig. 26 shows the temperature and pressure profile of the sintering trials carried at the MIM facility. Various isothermal holds were applied; (i) 400C for 12 hrs, (ii) 450C for 3 hrs, (iii) 600C for 3 hrs for effective thermal debinding. In addition, a low pressure of 300 torr during thermal debinding was maintained to allow the binders to easily come out of the printed samples, under flowing H2 condition. The aim of thermal debinding is to remove various

backbone polymeric binders by converting them into gaseous hydrocarbon species. Forming hydrocarbon products happens more effectively under flowing H2 with a low pressure. For high temperature sintering, two conditions have been tried, (i) under vacuum, and (ii) under flowing hydrogen environment with a pressure of 600 torr. In addition, two isothermal holds were applied, one at 400C for 12 hours for thermal debinding and another at 1300C for 1.5 hours for high temperature sintering (Fig. 26b).



Fig. 26 Pressure and temperature profile at MIM facility, (a) trial-II, (b) trial-I

Coupon samples after sintering at the MIM facility were imaged and shown in Fig. 27. During trial-I run, most of the MEAM-printed samples were not able to retain shape, which could be due to a variation in binder content. Samples made from the filament SETO23_1 melted and formed puddles, while those from SETO23_3 retained their shape and structural integrity. SETO23_5 samples lost shape but to a lesser extent than SETO23_1. This behavior is linked to the composition of the filaments: SETO23_3 has the lowest amount of polypropylene (PP) and includes HDPE, while SETO23_5 has reduced PP. There appears to be a threshold for PP content, above which samples lose shape completely. SETO23_3 samples also showed surface bubbles, likely due to binders evaporating. In comparison, samples sintered during trial-II runs made using filament containing FeCrAl powder content to 65%, and PP as the only backbone binder up to 25% by volume, showed less melting issue. Also, it appears that the vacuum run samples performed better in terms of shape retention, polymer bubbling out and overall appearance of the sample.



Fig. 27 Images of SSAM-fabricated 3-D shapes that were sintered at a commercial MIM facility during BP2Q2 and BP2Q3

Density of samples sintered has been measured by Archimedes' principle and was additionally confirmed by optical imaging and micro-CT methods. For density measurement using Archimedes' principle, weight of the samples in air (W_a) and while submerged in deionised water (W_w) were obtined and the density was caculated using the formula below where C is the density of DI water at the temperature (0.99843 g/cc).

$$Density, \rho = \frac{W_a * C}{W_a - W_w}$$

To obtain the density using image processing, 5 optical images of taken from the center of the sample wer analyzed using image thresholding feature of ImageJ software. Table 15 provides a summary of density numbers noted for various SSAM-printed samples made during BP2Q3. Overall, it appears that coupon samples printed using SETO 23_15 shows higher density compared to samples printed using SETO 23_14. Archimedes method shows density of ~95-96% when sintering is carried out under vacuum. Optical imaging indicates the density number to be ~98% or higher, for these samples. 6 mm dia. FeCrAl pressed pellets, used as control, confirms density measurement method. In comparison, SSAM-printed samples sintered under flowing H2 shows a lower density of ~80-85%.

	Archimedes' Density		Density through image processing	
Sample	vacuum	Hydrogen	vacuum	Hydrogen
15-90-0.15	NA	81.7%	98.6%	NA
15-90-0.3	96.7%	83.0%	98.5%	NA
15-95-0.15	96.3%	82.1%	98.5%	NA
15-95-0.3	NA	79.0%	98.8%	NA
15-100-0.15	95.5%	83.4%	98.4%	NA
15-100-0.3	83.7%	88.4%	98.4%	NA
14-90-0.15	96.2%	85.6%	98.2%	NA
14-90-0.3	92.9%	91.0%	98.1%	NA
14-95-0.15	NA	89.2%	98.5%	NA
14-95-0.3	NA	76.8%	98.2%	NA
14-100-0.15	94.2%	87.0%	98.9%	NA
14-100-0.3	NA	90.6%	96.2%	NA
pure AM100 batch 2 pressed pellet 6 mm	95.4%	NA	99.5%	NA

Table 15. Density data for MEAM-printed samples sintered at MIM facility, trial-II

Optical images of cross-section along thickness direction of SSAM-printed samples sintered under vacuum are summarized in Table 16a and Table 16b, for SETO 23_14 and SETO 23_15 filaments. The images clearly show the effect of print parameters. A layer height of 0.15 mm results in formation of macro-porosities at similar intervals of length which were not present in the samples with layer height of 0.3 mm. This can be corelated to the cross-section images of the green samples. Alternate, adjoining print lines along the length direction were joint together in the samples with the layer height of 0.15 mm. On the other hand, the samples with the layer height of 0.3 mm had periodic gaps between the printed layers. The periodic gaps would allow binders to escape during thermal debind, and result in better densification during high temperature sintering.

Table 16a MEAM-printed sample optical microscope image (after sintering)	

SETO 23_14	0.15 mm layer height	0.3 mm layer height		
sinter montage				
90% infill				
95% infill				
100% infill				

SETO	0.15 mm layer height	0.3 mm layer height
23_15		
sinter		
montage		
90%		
infill		
95%		
infill		
100%	Restriction (Fr	Randonini Ya
infill		

Table 16b MEAM-printed sample cross-section optical microscope image (after sintering)

Determination of internal voids that may be present in SSAM-printed coupons were further characterized by carrying out micro-CT. Micro-CT provides a quick, non-destructive method of examining internal void structure, and it proved quite helpful to find out the internal structure for SSAM-printed coupons. Since micro-CT captures an image of the printed sample along the X-ray beam penetration direction, it provides information about pores that are present spatially, which will not be determined by a single random cross-section imaged using optical microscopy. Micro-CT images of sintered samples made by SETO 23_14 and SETO 23_15 are summarized in Table 17a and Table 17b, respectively. High degree of densification is confirmed from micro-CT data for samples printed using SETO 23_15 filament with 95% infill and 0.3 mm layer height.



Table 17a. Micro-CT image, after sintering (SETO 23_14)



Table 17b. Micro-CT image, after sintering (SETO 23_15)

A comparison of low and high magnification SEM images of the best and worst composite sample and the pressed pellet, which serves as the control sample is presented in Table 18a and 18b. It clearly shows the marked improvement in densification of the pressed and printed FeCrAl samples in all the conditions. This improvement is attributed to both changes in filament chemistry where the metal loading has been increased from 55 to 65% in the printed samples, optimization of print parameters and sintering conditions, including temperature, time and environment.

Low sintering (1300C 1.5h H2) magnification images-SEM		sintering (1360C 6h vacuum)	
Pure FeCrAl pressed pellet	50 160 KW W0 101 Fem 564-673.0 160Mic (2010) 90 μπ	310 160 ₩ 199 8лла 170 180 ₩ 99 8лла 170 181 184/9 8ла2	
MEAM-printed FeCrAl (I)		CO 100.W W0.93 pm Get 1473/2 Highlight @1000 50 pm 110 114/2 Alg/Co.2022 Get 1473/2 Highlight @1000 50 pm	
MEAM-printed FeCrAl (II)	TO THOSE WELLERS SERVICE LEAVE (LEAVE (LEAVE (LEAVE)))	100 INDER WORSTAM - SALETSSO Haynes (\$750) - Soyan	

Table 18a. Low magnification (500X) SEM images after sintering at MIM facility

High magnification images-SEM	sintering (1300C 1.5h H2)	sintering (1360C 6h vacuum)		
Pure FeCrAl pressed pellet	SPD BD AV WE 101 Ferm Sel - FC 720 Henne Sel - S	870 180.W. W05.Merrer. 364. FC756 Hankle: @04.000 90.mt		
MEAM-printed FeCrAl (I)	CO BORY WORLAWS SAFE 765 BANK GROOT	50 160.kV W0 %4yrm Sol JC750 Highline: @10,000 10 µm 10 164 Algo Salazz Sol JC750 Highline: @10,000 10 µm		
MEAM-printed FeCrAl (II)		50 Hoav WD837mm Sou FC726 Heynold (0)-200 40 pm		

Table 18b. High magnification (2000X) SEM images after sintering at MIM facility

Based on the density measurement data and SEM imaging, it appears that better densification in MEAM-printed FeCrAl coupons are achieved by (i) use of high temperature sintering (>1300C) under vacuum, (ii) use of 100% fine FeCrAl powder used in making composite filament, and (iii) use of 95% infill and 0.3 mm layer height as an optimum print condition.

4.0 Microstructure of sintered MEAM-printed FeCrAl samples

One of the advantages of using MEAM, currently investigated SSAM method, is that it does not involve melt and rapid solidification of the feedstock FeCrAl powder. Therefore, the microstructure does not consist of dendritic grains or columnar grains along laser raster. Densification of MEAM-printed 3-D shapes takes place during high temperature sintering, where diffusion in the solid state is the underlying mass transport mechanism. As a result, the final microstructure is an equiaxed grain structure, isotropic, and lacks any preferred orientation. Such microstructural features are beneficial to achieve isotropic mechanical properties, which is hard to obtain in melt-solidification AM methods. Further, densification by solid state diffusion process preserves homogeneous distribution of oxide dispersion phases that are added for strengthening. The investigated FeCrAl alloy contains a small amount reactive elements (Ti, Zr, Y etc.) added that form fine scale (~nm) oxides during high temperature treatment. Presence of these fine oxide dispersion phase provides strength to an otherwise soft alloy, and more importantly, dispersion strengthening can be retained at an elevated temperature since the oxides are stable in nature, and do not dissolve back into the alloy unlike precipitates do. However, to attain high degree of dispersion strengthening, it is critical that the uniform distribution of fine ~nm scale oxides need to be preserved. Meltsolidification AM methods typically destroys such uniform distribution of oxide phases. SSAM methods such as MEAM can preserve the distribution of oxide phases needed for high temperature strength in oxide dispersion strengthened (ODS) alloys, such as ODS-FeCrAl alloy used in this research.

Backscatter SEM images from sintered pressed pellets are shown in Figure 28. Spherical nature of the starting FeCrAl feedstock is apparent in Figure 28a. Sintering up to 1000 °C does not change the morphology of the starting feedstock powder. First signs of shape change is noted after sintering at 1250 °C. Change in grain size as a function of sintering temperature is reported in Figure 25e. There is not much change in the grain size, and it stays below 10 μ m even after sintering at 1250 °C, which shows remarkable thermal stability of AM100 FeCrAl powder feedstock.



Figure 28. SEM images of pressed FeCrAl powder pellets. (a) as-pressed, (b) Pressed pellet heated at 700C for 4 hrs (c) pressed pellet heated at 1000C for 4 hrs, (d) pressed pellet heated at 1250C for 2.5 h (e) plot of grain size as a function of sintering condition

Grain structure of MEAM-printed FeCrAl cuboid pellets is summarized in Figure 29. The equiaxed nature of the AM-printed pellets is immediately clear from these images. This is in contrast to typical elongated grain structure morphology observed in melt-solidification based AM methods. Depending on the sintering temperature and time, the final grain size is noted to vary between ~15-25 μ m, as reported in Figure 29f.



Figure 29. Grain structure of sintered SSAM-printed FeCrAl pellets, (a) 1250C, (b) 1300C, (c) 1325C, (d) 1350C, (e) 1380C, (f) grain size chart

The equiaxed nature of grains in the sintered condition is further confirmed by EBSD analysis. A low magnification EBSD map of a MEAM-printed FeCrAl sample sintered at 1350 °C is shown in Figure 30a. It shows the equiaxed grains. Figure 30b shows an inverse pole figure proving the absence of any texture in the sintered sample which would result in favorable properties. The corresponding grain size distribution is shown in Figure 30c. It shows that most of the grains are sized at about 25- μ m diameter and the grains range from 3 to 124 μ m in size.



Figure 30. EBSD analysis of SSAM-printed sample sintered at 1350C, (a) EBSD map b) Inverse pole figure c) Histogram of grain diameter of the sample in (a)

MEAM-printed samples sintered at the commercial MIM facility were also studied using TEM to investigate its ODS microstructure. TEM data from the printed FeCrAl sample have been shown in the fig 7 below. The spot TEM-EDS map and spot scan confirm the presence of nanoscale Yttrium oxides, showing the effectiveness of MEAM method in preserving ~nm oxides.



Fig 31: TEM-EDS spot analysis and TEM-EDS map analysis from the sample sintered in BP2Q2

5.0 Mechanical properties of MEAM-printed FeCrAl samples

To evaluate the mechanical integrity and strength of the sintered samples, Vickers microhardness tests were conducted using an indent load of 500gf for 12 seconds. Comparison of hardness of samples from various sintering trials is presented in fig. 32. The MEAM-printed samples from MIM facility sintered at 1360C for 6h in vacuum shows an increase in hardness by atleast 23% (compared to the sample sintered at 1350C). These results are very promising and indicate towards much better mechanical properties.



Fig 32: Micro-hardness data from samples sintered in BP1 and BP2.

Uniaxial tensile properties at room temperature have been determined for (i) pressed and sintered FeCrAl blank, and (ii) MEAM-printed and sintered FeCrAl blanks. Miniature-sized tensile test samples have been used to determine the tensile properties. Room temperature tensile tests were conducted at a strain rate of 2 x 1E-4/s. Fig 33 shows the tensile coupon geometry used to determine mechanical properties of MEAM-printed FeCrAl samples.



Fig. 33 Miniature test coupon geometry and sample orientation; (a) pressed and sintered FeCrAl blank, (b) SSAM printed and sintered blank in XY plane, (c) test setup

Test summary is captured in Table 19, which indicates high tensile strength (TS) in pressed + sintered condition (640 MPa, 97% of Kanthal provided data on this alloy). In MEAM printed

+ sintered condition, highest TS noted is ~600 MPa, 91% of Kanthal provided data. % elongation to failure is lower in the case of MEAM printed samples, indicating need for further process optimization. Fractography has been carried out for the following two samples (highlighted) in Table 19.

	Specimen label	Orientation of GL	# Samples	Tensile Strength (MPa)
1	15-95-0.15-B (MEAM print + sinter)	XY	2	589.3
2	15-95-0.3-C (MEAM print + sinter)	XY	2	603.2
3	15-100-0.15-B (MEAM print + sinter)	XY	2	596.6
4	1.5 MT 45ksi CIP vacuum (MIM facility)	х	2	633.7
5	3.6 MT 45ksi CIP vacuum (MIM facility)	х	2	639.9
7	1.5 MT 45ksi CIP Hydrogen (MIM facility)	х	2	629.6
6	3.6 MT 45ksi CIP Hydrogen (MIM facility)	х	2	599.5
8	1.5 MT 45ksi CIP vacuum (in-house)	х	2	638.6
9	3.6 MT 45ksi CIP vacuum (in-house)	x	2	580.0
10	Kanthal supplier data	x	x	660.0

Table 19. Room temperature tensile test summary

Fractured sample from tensile sample that was machined from printed and sintered sample, was examined under SEM, as shown in Fig. 34. This SSAM-printed sample was sintered at 1360C for 6 hrs under vacuum. The fractured surface shows ductile fracture with multi-void coalescence. The sample also shows a print defect at the center of the sample which could have resulted in lower ductility. A longitudinal cross-sectional of the same failed sample is shown in Fig. 35 to get a better idea about internal structure. it appears that there are occasional elongated voids within this sample, and also some serrations at the sample edge. Both features are possibly leading to reduced tensile ductility. Fig 36 shows the fractured sample from tensile sample that was machined from CIPed and sintered blank. Compared to SSAM-printed sample, the pressed and sintered sample shows reduced degree of ductile fracture features. Presence of quasi-cleavage fracture is evident in the pressed and sintered sample, typical of ferritic steels.



Fig. 34 Fractured surface from tensile tested sample that was machined from printed and sintered brick. (15-95-0.3-C (MEAM print + sinter))



Fig. 35. Optical image of the longitudinal cross-section of SSAM-printed and sintered tensile sample after failure. Elongated voids are present together with serrated edge.



Fig. 36 Fractured surface from tensile tested sample that was machined from CIPed and sintered pellet. (3.6 MT 45ksi CIP vacuum (MIM facility))

Finally, room temperature mechanical strength of ODS-FeCrAl alloy studied in this research has been compared against some of the conventional structural alloys to get an idea about its comparative performance. Other alloys that were tested include (i) Ni-base Inconel 625, (ii) Kanthal APMT – a wrought version of FeCrAlMo alloy, and (iii) 316L stainless steel (SS). The engineering stress-strain plot is shown in Fig 37. Inconel 625 shows the highest tensile strength and high ductility. 316L SS is the weakest alloy but has the highest ductility. FeCrAl alloys perform in between these two alloys, in terms of both strength and ductility. In addition, sintered AM100 alloy (ODS-FeCrAl alloy studied in this research) shows very good ductility, being very similar to wrought Kanthal APMT alloy. This observation confirms that we were able to achieve very high degree of densification through our vacuum sintering technique in ODS-FeCrAl alloy. Further material research using SSAM method should be conducted to harness the performance and cost benefits of FeCrAl alloys.





6.0 Fabrication of larger parts through MEAM

In the last phase of this research, we aimed at printing relatively larger parts using optimized composite FeCrAl filaments (65% vol. loaded fine FeCrAl powder mixed with PP-PW-SA). For printing, optimized print parameters (95% infill and 0.3 mm layer height) were used. Debinding and sintering was done by (i) solvent debind in cyclohexane, and (ii) thermal debind and sinter at MIM facility using most optimized sintering condition (1360C, 6 hrs, vacuum).

In addition, we designed and printed modular components to explore manufacturing larger parts using MEAM. A simple honeycomb design was selected to try modular printing effort. These components are intended to connect and bond during sintering to form a solid piece. While a mechanical bond would enhance strength, challenges arose with complex designs, such as overhangs and fine features like threads, which could deform during printing. To support large overhangs, a second extruder with dissolvable material may be needed to achieve high-quality prints. As an alternative to mechanical interfaces, we designed the components to nest together, aligning channels for better bonding. Protrusions were intentionally oversized for a better fit and were sanded down before solvent debinding. Solidworks drawing of this approach and actual printed parts in green state are shown in Fig. 38. MEAM-printed modular pieces, after high temperature sintering, got bonded together. Cross-sectional microscopy confirmed success of sinter-bonding method. However, further process design and process optimization is needed to ensure completely void-free bonding at the interface of these modular pieces (Fig. 39). Given, it was our very first trial at sinter-bonding method with a reasonable success, we believe modular design through MEAM and subsequent sinter-bonding could be a good strategy to fabricate large parts by MEAM method.



Fig. 38 Modular SSAM-printed FeCrAl honeycomb shape. (a) individual modules, (b) three modules stacked together



Fig. 39 Modular SSAM-printed FeCrAl honeycomb shape after sintering. (a) low-magnification cross-section, (b) interface showing signs of sinter-bonding, additional optimization needed to remove voids, (iii) 100% dense matrix

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Pacific Northwest National Laboratory

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