Chapter 6 – Characterization of Two Gradient Alloys Fabricated by Laser Engineered Net Shaping

Additive manufacturing is a relatively new field based around the idea of depositing one layer of a material at a time in order to build a three dimensional structure. It is also commonly known as rapid prototyping or 3D printing. Typical additive manufacturing processes begin with a computer-designed part. A layering path is then generated by software, and is input into the machine to build the part. Traditional machining processes require removal of material in order to create a final shape. Additive manufacturing works in the reverse, only depositing material required for the finished product. It also provides extra flexibility, allowing for hollow, low density, or blind structures to be manufactured, features that are difficult or impossible to obtain with traditional machining.

A variety of additive manufacturing processes have been developed recently. The most common technique is known as fused deposition modeling (FDM). A thin filament is pushed through a heated nozzle which can be positioned in an x-y plane. Either the nozzle or build surface is then moved after each layer. The filament is most commonly made out of a polymer, although variants which use metal feedstock are also under development. Surface finishes range from very rough to smooth, and are often directly related to the price of the printing machine and the total size of the smallest feature. Resolution can also be sacrificed to increase printing speed by increasing layer thickness.

Another common technique is photopolymerization. In this case, a tank with a build platform near the surface is filled with a photosensitive polymer solution. A laser is then used to activate desired sections and instigate polymerization. The build table is then lowered, and the next layer is polymerized. This technique can offer high quality surface finishes, but tends to be slow and can only be used with polymers. A third technique involves using powders as feedstock material, and there are three variants; in one version a powder is mixed with a binder and printed similar to FDM above. After printing, the final product can be sintered or thermoset. This results in a good quality surface, but it is not fully dense or necessarily mechanically robust. A second version, called direct metal laser sintering, is similar to photopolymerization, except instead of using a pool of liquid it employs a base layer of metallic powder.¹ A powerful laser is then used to melt the desired areas, a new layer of powder is added, and the process is repeated.

The technique used in this study, laser engineered net shaping (LENS), uses a nozzle to inject metallic powder into the laser. This removes the need for a bed of metallic powder, so only the powder to be melted is needed. Another benefit of LENS is the production of fully dense parts. This is because it melts powder instead of using sintering for consolidation. Figure 6-1 contains a schematic of the LENS machine used in this study, which has been outfitted with four nozzles, each capable of feeding from a different hopper (as shown in Figure 6-1a). This technique has been used in the literature to fabricate samples transitioning from one alloy to another; however, previous research largely focused on studying hardness and dislocations, not the formation of the gradient..^{2–4}

In this study, pillars were made which transition from Ti-6Al-4V to pure vanadium. They were printed on a Ti-6Al-4V plate, with the Ti-6Al-4V deposited first, and transitioning to V on top. Figure 6-1b shows a pillar during the build process. Figure 6-1c and 6-1d show the completed structures. Table 6-1 outlines the parameters for building the pillar. Each layer was 0.38 mm thick; steps were done in 3% volume increments. Each composition was five layers thick, and a total of 195 individual layers were deposited over 585 minutes. The laser's power was held at a constant 600 W, with 4.4 LPM of argon gas flowing. The build process was done in a series of small, linear steps to minimize microstructural differences from one layer to another.

This proved to be a successful technique, as compared to other pillar composition gradients, which suffered failures in transition regimes that had larger changes in composition (as much as 25% different) from one layer to the next.



Figure 6-1: Schematic of the laser deposition (LD) building heads used to fabricate gradient alloys. **(b)** Image of the LD process fabricating several test specimens of the Ti-V gradients. **(c)** Three gradient alloy specimens; a hollow cylinder, a plate and a beam. **(d)** Example of a "forest" of gradient alloy posts used to vary gradient compositions.

Lavors	% vol	% vol	g/min	g/min
Layers	Ti-6-4	V	Ti-6-4	V
0-28	100%	0%	2.1	0
29-33	97%	3%	2.04	0.08
34-38	94%	6%	1.97	0.16
39-43	91%	9%	1.91	0.24
44-48	88%	12%	1.85	0.31
49-53	85%	15%	1.79	0.39
54-58	82%	18%	1.72	0.47
59-63	79%	21%	1.66	0.55
64-68	76%	24%	1.59	0.63
69-73	73%	27%	1.53	0.71
74-78	70%	30%	1.47	0.78
79-83	67%	33%	1.41	0.86
84-88	64%	36%	1.34	0.91
89-93	61%	39%	1.28	1.02
94-98	58%	42%	1.22	1.1
99-103	55%	45%	1.16	1.18
104-108	52%	48%	1.09	1.26
109-113	49%	51%	1.57	2.03
114-118	46%	54%	1.52	2.15
119-123	43%	57%	1.42	2.27
124-128	40%	60%	1.32	2.39
129-133	37%	63%	1.22	2.51
134-138	34%	66%	1.12	2.63
139-143	31%	69%	1.02	2.75
144-148	28%	72%	0.92	2.87
149-153	25%	75%	0.83	2.99
154-158	22%	78%	0.73	3.11
159-162	19%	81%	0.62	3.23
163-166	16%	84%	0.53	3.35
167-170	13%	87%	0.43	3.47
171-174	10%	90%	0.3	3.58
175-178	7%	93%	0.23	3.71
179-182	4%	96%	0.13	3.83
183-186	1%	99%	0.03	3.94
187-195	0%	100%	0	3.98

Table 6-1: Build conditions for the Ti-6Al-4V gradient alloy.

The gradient alloy used in this study was chosen to provide a structure which would be high-strength and low-density at one end and have a high melting point at the other. An example of where such a design would be ideal is a rocket nozzle transitioning directly into the body, eliminating the need for a joining process between the two.

X-ray diffraction (XRD) was performed to verify successful fabrication, and to determine which phases were produced. The pillars were serial sectioned on an Allied Techcut 5 laboratory saw. The face of each sample was inspected via XRD to determine the phases present in its microstructure.

Standard Ti-6Al-4V is a mixture of both α (hcp) and β (bcc) crystal structures, while elemental vanadium is purely bcc. Figure 6-2a is a binary phase diagram of titanium and vanadium. A large, single phase bcc region is seen at elevated temperatures, with only minimal solubility of vanadium into the hcp phase. In equilibrium at temperatures below 873 K, a two phase mixture is expected for compositions ranging from roughly 5% to 90% vanadium. This is supported by the ternary phase diagrams of Ti-Al-V given at 600 K, 900 K, and 1200 K (Figure 6-2b-d, respectively). A representation of the path taken through the alloy is drawn on the ternary phase diagrams. The transition of Ti-6Al-4V to vanadium was chosen since it thermodynamically avoids any intermetallic phases. Another low density, high strength alloy is Al-2024. However, the transition from a predominantly aluminum alloy to vanadium would cross through a number of intermetallic phases. For aluminum to vanadium, the alloy would start as fcc, then change to a stoichiometric fcc, tetragonal, monoclinic, hexagonal, and body centered cubic phases, followed by bcc vanadium.⁵ All of these different crystal structures create all sorts of different interfaces and wildly different mechanical properties within the material. By choosing to transition from predominantly titanium to vanadium, much of this issue is avoided.



Figure 6-2: (a) A binary Ti-V phase diagram. α is hcp and β is bcc. (b) Ternary Ti-Al-V phase diagram. The addition of aluminum to the system appears to broaden the two phase region slightly. The outlined path demonstrates the compositions contained in the tested pillar.^{6,7}

Of course, real manufacturing processes do not always wind up with what is expected from thermodynamic equilibrium. Figure 6-3b was constructed by serial-sectioning a pillar and performing XRD on each surface. At the pure Ti-6Al-4V side, only the hcp α is visible. After only a few layers, bcc peaks also begin to appear and coexist with the hcp phase. By only ~15% of the way to pure vanadium, all hcp peaks have disappeared and only bcc remain. This does not match up with the results predicted from the phase diagrams in Figure 6-2. It is actually closer in line to the equilibrium phase compositions seen at 900 K in the Ti-Al-V ternary phase diagram. However, since these materials are deposited layer by layer, it is likely they experience a fairly rapid quench rate. Therefore, they won't have time to reach an equilibrium state. Individual XRD patterns are shown in Figure 6-3c(i-v). (i) is pure Ti-6Al-4V, but only contains bcc. (ii) has the



Figure 6-3: (a) A hardness vs position plot for the Ti-6-4 to V sample. (b) 3d mapping of XRD intensities across the sample. A slow change in diffraction angles is apparent in the BCC phase. (c) Indexed diffraction patterns identified to in (a). The coexistance of both HCP and BCC phases is demonstrated.

beginning of bcc presence, and (iii) has diminishing levels of hcp. By (iv) only the bcc phase exists, and that continues all the way through (v).

Figure 6-3a shows more evidence for the gradual changes of phase. Initially, in the Ti-6AI-4V region (i), the hardness is roughly 440 Brinell. In the two phase region (ii and iii) the hardness is increased to a maximum of 500 Brinell. By (iv), when only bcc is present, the hardness fluctuates around 300 Brinell. It then trails off to vanadium's normal value of 160 Brinell.

As mentioned above, having minimal crystal structure changes is desirable in a gradient alloy. Likewise, having a small, gradual, change in lattice parameter would likely mean fewer weak interfaces between layers. It is subtle, but in Figure 6-3, a shift in the position of the diffracted peaks is demonstrable. It is most visible in the (211) bcc reflection in Figure 6-3b. By indexing each peak, and using Bragg's law, it can be shown that,

$$2d_{hkl} \sin(\theta) = n\lambda$$

$$d_{hkl} = \frac{n\lambda}{2\sin(\theta)}$$
(1)

where *n* is the number of wavelengths, λ is the wavelength of the incident x-rays, θ is the angle of the source to the surface of the sample, and d_{hkl} is the interplanar spacing for planes with indices *h*, *k*, and *l*. In bcc metals, the first set of Bragg reflections expected are (110), (200), and (211). The relationship between a measured d_{hkl} and a_o for a bcc material is

$$\frac{1}{d_{hkl}^{2}} = \left[h^{2} + k^{2} + l^{2}\right] \frac{1}{a^{2}}$$

$$a_{0} = d_{hkl} \sqrt{h^{2} + k^{2} + l^{2}}$$

$$a_{0} = \frac{n\lambda}{2\sin(\theta_{hkl})} \sqrt{h^{2} + k^{2} + l^{2}}$$
(4)

For hcp the measured reflections are (100), (101), (102), (110), (103), (200), and (112).

$$\frac{1}{d_{hkl}^2} = \left[\frac{4}{3}\left(h^2 + k^2 + hk\right) + l^2\left(\frac{a}{c}\right)^2\right]\frac{1}{a^2}$$
(5)

For planes (*hk0*) and (*001*).

$$a_{0} = 2d_{hk0}\sqrt{\frac{h^{2} + k^{2} + hk}{3}}$$

$$a_{0} = \frac{n\lambda}{\sin(\theta_{hk0})}\sqrt{\frac{h^{2} + k^{2} + hk}{3}}$$
(6)

$$c_0 = l \cdot d_{00l}$$

$$c_0 = l \frac{n\lambda}{2\sin(\theta_{00l})}$$
(7)

By collecting all of this, and finding the volume for each unit cell $(a_0^3 \text{ for bcc and } a_0^2 b_0 \text{ for hcp})$, Figure 6-4 was generated. A steady change in lattice parameter can be seen as V is added to Ti-6Al-4V. The unit cell's volume increases at a rate of 6.3e-2 Å³/(vol %); a_0 increases at a rate of 2.3e-3 Å/(vol %) for the bcc crystals. Once the dual phase region is entered, the bcc lattice shrinks slightly while the hcp unit cell is larger. The shrinkage is due to the decreased amount of titanium dissolved in the vanadium bcc crystals. These results are promising, as there is a slow, gradual change in lattice parameter even when there is a transition involving two phases present at the same time.



Figure 6-4: Volume of a unit cell versus composition. As more titanium is added, an increase in cell volume can be seen. Beta-titanium has a larger lattice constant than vanadium (3.282 Å for Ti versus 3.020 Å for V), so this expansion is reasonable.

The next alloy synthesized was fabricated in two geometries. The first was a radial gradient deposited on a central A286 stainless steel rod. It transitions from 304L stainless steel at the core to Invar 36 at the perimeter, as seen in Figure 6-5. The alloy was fabricated by rotating the central A286 cylinder along one axis while the build head slowly moved along the axis perpendicular to the plane of rotation. The second geometry grown was square pillars, the same as the Ti-6Al-4V to vanadium. In this case, the 304L steel was deposited onto 304L stainless steel plate with Invar 36 at the free end. This gradient alloy was chosen, as it offers a very common and versatile material (304L) which is high in strength, and can be welded and readily machined. Invar provides a surface layer with little to no thermal expansion.



A situation where this combination of properties is useful is mirror mounts used on satellites in space. Mirrors used in space applications frequently consist of a quartz substrate that has been silvered on one side. The quartz has a negligible coefficient of thermal expansion (CTE). If the mount holding the mirror's CTE does not match the mirror substrate's CTE, then the mirror will experience a torque and deform. In high performance systems, this slight deflection can significantly degrade the optic system. An obvious solution would be to make the entire mount of Invar. Then the problem of connecting the mount to the main structure arises. If the mount is entirely made of Invar, it cannot be welded. Therefore, bolts would have to be used, but there is then a CTE mismatch between the mount and bolt used to attach it. By transitioning within the mount itself from Invar at the mirror end to stainless steel at the other, it can both act as an effective holder with zero CTE as well remain weldable to a steel support structure.

The radial gradient was designed with the intent to replace the current inserts for carbon fiber paneling. Panels are currently manufactured using a cladding of carbon fiber around aluminum honeycomb panels (Figure 6-6). These are used for their high stiffness and low density. However, in order to attach the panels together, or to other structures, threaded metal inserts are epoxied into the panels. These panels are often subjected to extreme temperatures with large fluctuations, and undergo significant thermal cycling. The carbon fiber face sheets have a near-zero CTE, while the steel inserts have a high CTE. The radial gradient was designed such that the threading would be the same material as that used for the bolts which would attach to it. There is then a rapid transition to Invar to minimize the expansion of the insert as a whole to protect the carbon fiber from expansion. Figure 10a is a collection of fully finished inserts. Figure 6-6c is before and after a pullout test. Rupturing of the carbon fiber face sheet is visible.



Figure 6-6: (a) Printed and machined inserts for carbon fiber and aluminum honeycomb sheets. (b) An insert installed into a panel. (c) Before and after a pull-out test.

Thermodynamically, this is also an ideal system to attempt, as both alloys are primarily iron with significant amounts of nickel. 304L contains approximately 20% chromium, 10% nickel, and 70% iron.⁸ It is an austenitic grade of stainless steel. Similarly, Invar 36 is fcc iron, which is the austenite phase. As seen in Figure 6-5c, it contains 64% iron and 36% nickel. The gradient path is highlighted on the ternary phase diagram. The only phase which should be produced through the entire sample is austenitic fcc.

Determination of phases present was done via XRD in a manner similar to the Ti-6Al-4V to vanadium pillar above. It was sectioned in the manner shown in Figure 6-7. Each of the six XRD scans are also shown in the figure. Only fcc peaks are seen, and there is no apparent shift of peak positions. This is a great result, as it means the lattice has changed minimally, and the amount of strain and deformation experienced by the lattice should be minimized.

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Figure 6-7: X-ray scans were obtained for the radial sample as well as for the linear sample of 304L to Invar 36. The radial alloy was sectioned according to the map above and x-ray scans were performed on each section, shown at right. Only the austenite phase was detected.

In order to estimate the CTE throughout the gradient, two mixed-composition pillars were fabricated. They were then machined into 2-3 mm tall cylinders with an aspect ratio of, at most, 2:1. The faces were polished to be plane parallel. The samples were tested in a Perkin-Elmer Diamond TMA with a static applied force of 100 mN. They were then repeatedly cycled from room temperature to 773 K. A representative thermal cycling measurement is shown in Figure 6-8a. Multiple cycles were used, since typically the first heating cycle is needed to ensure the sample is properly seated in the testing apparatus. The following heating and cooling cycles all overlay consistently. In order to find the CTE from a position versus temperature plot the instantaneous slope is determined for each point and then plotted versus temperature.



Figure 6-8: (a) A representative thermal expansion measurement plotting probe position vs. temperature. The first cycle was always discarded since it was used to "seat" the sample properly under the load. (b) Expansion of the cylinder versus temperature. Four of those measurements are shown, one from the Invar side of the gradient, one from the steel side, and two samples near the Invar side of the gradient. Sample 2 represents the sample most near the pure Invar, and Sample 3 is the next sample beyond that. (c) The CTE was obtained by differentiating the curves from (b).

A strong correlation between composition and CTE was measured. Figure 6-8b is a plot of probe position versus temperature across a very large temperature range. Invar 36 and SS 304L are the "pure" alloys, while Sample 2 is 90% Invar 36 and Sample 3 75% Invar. Near room temperature very different expansion behaviors are seen. Invar 36 initially shrinks, stays constant for a small range, and then begins expanding. On the other hand, the other three samples all monotonically expand. Figure 6-8c is the result of taking derivatives of the above curves. Invar 36 is again seen to initially have a slightly negative CTE, having its actual CTE of zero around 52° C, and continuing to a CTE of 5 ppm. Sample 2 begins with a moderate CTE of 6.5 ppm and grows to 13.5 ppm by 100° C. Sample 3 starts at 11.3 ppm and increases to 17 ppm. 304L is 14.5 ppm initially, and, like Sample 3, has a final CTE of approximately 17 ppm. Figure 9c gives the total change in CTE as well as the change in CTE per degree Celsius. Invar 36 has the largest change, at 7.84 ppm/K, and 304L has the least at 2.12 ppm/K. Both of the intermediate alloys have a smaller change in CTE than Invar. The alloy having greater Invar composition having the greater sensitivity to temperature. The CTE properties measured for all compositions of the gradient alloy demonstrate that it is possible to tailor the CTE of an alloy by mixing known materials. It is likely with sufficiently small steps, a completely tailored CTE could be achieved.

Composition	ΔCOE	d COE d T
	(ppm/K)	(ppm/K²)
Invar 36	7.84	0.12
Sample 2	6.94	0.10
Sample 3	5.47	0.081
SS 304L	2.12	0.032

Table 6-2: Linearized CTEs and change in CTE from ambient temperatures to 373 K

In this chapter, the feasibility of fabricating two different gradient alloys was demonstrated. By careful selection of the alloys to be deposited, unwanted phases were able to be avoided. Confirmation of the correct phases being present was demonstrated via XRD. The tunability of the coefficient of thermal expansion of the 304L – Invar system was also demonstrated.

Collaborators on this project include Joanna Kolodziejska from Caltech/JPL for the illustrations in Figure 6-1 and Figure 6-5, Richard Otis from Penn State for the phase diagram in Figure 6-5, and John Paul Borgonia from JPL for being the driving force behind this project, fabricating all of the structures used in this study.

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