CONTROLLING PHASE COMPOSITION IN SELECTIVE LASER MELTED STAINLESS STEELS

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Abstract

Commercially important stainless steels can be austenitic or martensitic and this phase composition fundamentally controls the mechanical properties of the material. With selective laser melting (SLM), 17-4 stainless steel can be produced in either phase depending on powder composition, SLM conditions and post-build heat treatment. This behavior is examined using optical and electron microscopy and high temperature x-ray diffraction in order to better understand the formation of metastable austenite and its transformation to martensite. Control of phase composition can produce a material with either extremely large strain-to-failure or high yield strength and can provide a method for completely eliminating residual stress.

Introduction

Stainless steel with a nominal composition 17% Ni, 4% Cr, 4%Cu is a common alloy for commercial, defense and medical applications. With conventional processing (casting and solution heat treating) the 17-4SS alloy is martensitic at room temperature and can be precipitation hardened to provide high yield strength and good elongation. Previous investigations with 17-4SS using SLM have reported various results with respect to as-processed phase composition. Facchini (2010) and Starr (2010) found that SLM produced a metastable austenitic material that cannot be hardened with standard heat treatment but that transforms to martensite during mechanical straining and exhibits exception elongation. Starr (2011) also reported that heating the as-process material to 788^{o}C and cooling produced martensite which could be hardening conventionally. More recently Murr (2011) found that the as-processed phase composition depends on the gas used during powder production and on the atmosphere used during the SLM process. Better understanding is needed both to ensure reproducible manufacturing of hardened stainless steel parts and, perhaps, to exploit the unique mechanical properties of the metastable austenitic form of this alloy.

Experiment

Stainless steel powders with nominal 17% Ni, 4% Cr were obtained from two sources: EOS (EOS GmbH, Munich, Germany) and LPW (LPW Technology USA, Maumee, OH). Both powders are formed using the gas atomization process with particle size and morphology suitable for use in the SLM process. The EOS powder was atomized in nitrogen, the "standard" atmosphere for stainless steel powder manufacturing. The LPW powder was a "special order" and was atomized in an argon atmosphere. Composition and particle size for the two powders are shown in Table 1.

Test specimens were created using an EOS M270 Dual Mode Direct Metal Laser Sintering machine, capable of operating under either nitrogen or argon atmosphere. All

specimens were fabricated using standard EOS-specified exposure parameters with a layer thickness of 20 or 40 micrometers. Exposure parameters for these two layer thicknesses are shown in Table 1.

Table 1. SLM exposure parameters

Layer (μm)	20	40
Power (W)	195	195
Speed (mm/s)	1000	800
Spacing (mm)	0.10	0.10
Energy density (J/mm^3)	98	61

Received powder and fabricated specimens were characterized by a variety of methods. The particle size distributions of the powders were measured using a Microtrac 3500 Particle Analyzer (Microtrac Inc, Montgomeryville, PA). Carbon and nitrogen content of EOS powders and fabricated parts were measured using combustion analysis (ASTM 1019-08) by IMR Metallurgical Services (Louisville, KY).

Powder morphology and dense specimen microstructure were observed using optical (Olympus MX 5) and scanning electron microscope (FEI Nova Nano SEM). The specimens for optical and SEM were prepared using standard metallographic specimen preparation methods. 10% oxalic acid electrolytic etching and modified Fry's reagent were used to etch the specimens.

Mechanical properties specimens were tested in tension using an Instron 5569A 50kN test machine (Norwood, MA) under displacement control at 1.0 mm/min. Stress-strain curves were obtained from load cell and strain gage output using Instron's Bluehill software.

The martensite content of fabricated specimens was measured by the magnetic induction method using a Feritscope FMP30 (Fischer Technology, Inc., Windsor, CT). This technique measures the total amount of ferritic phase in austenitic and duplex steel. The technique cannot distinguish between α-ferrite, δ-ferrite, and martensite (α′). For 17-4SS formation of ferrite is not expected and the Feritscope reading is assumed to the percentage martensite. Before each measurement session the instrument is calibrated against steel standards with 2.5, 10.5, 30 and 100% ferrite. Since the SLM materials are stainless steel the magnetic response is different than that of these carbon steel standards. A fully martensitic ("condition A") bar of commercial 17-4PH measured 75% ferrite.

X-ray diffraction analysis utilized a Bruker D8 diffractometer system with a dome-covered stage that allows heating of specimens in the range 30^o C to 1100^o C during data acquisition. For high temperature experiments a borosilicate glass slide was used over the ceramic heating element to prevent the x-ray diffraction pattern of this alumina stage from interfering with specimen pattern. Specimens for XRD analysis were cut parallel and perpendicular to the build plane using a low speed diamond saw and polished in three steps from course to fine culminating in a 0.5 micron diamond polished finish. After acquiring a room temperature pattern, each specimen was heated to a temperature of interest, held at this temperature for one hour and then cooled at 1^o C/s to 200^o C. Additional XRD patterns were obtained at fixed temperature over the range 200^o C to room temperature at 20^o C increments. The duration of each scan was roughly 11 minutes. The total time per run for each specimen was approximately three hours.

Results and Discussion

The results below show the effect of the SLM process and the post-build heat treatment on phase composition, microstructure and mechanical performance of 17-4 stainless steel.

As-received Powders

Table 2 shows the oxygen and nitrogen content of both powders. As expected, the EOS powder, atomized in N_2, has substantially more nitrogen than the argon-atomized LPW powder. Figure 1 shows XRD traces of the as-received powders. The EOS powder is mostly austenite (γ), while the LPW powder is mostly martensite (α'). Particle size and morphology of the two powders are similar - spherical (roughly) particles with diameters in the range 20-60 µm.

Table 2. Powder properties

		EOS	LPW
Comp-osition (wt%)	O	0.05	0.07
	N	0.15	0.03
Particle size	+62 µm	7.0%	7.4%
	+44 µm	42.7%	32.1%
	-23 µm	1.1%	8.9%

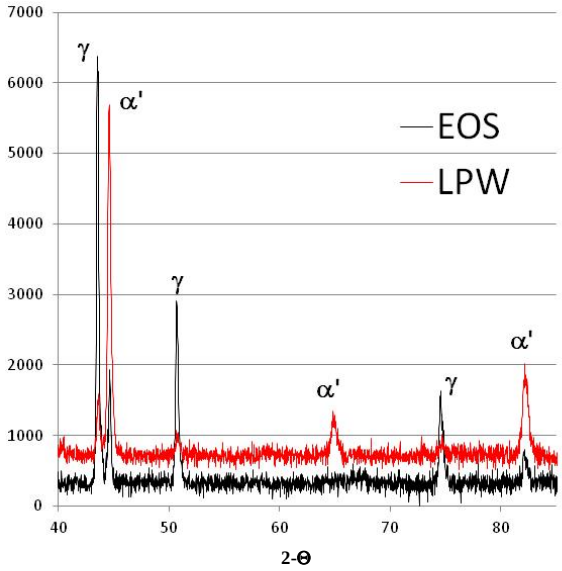

Figure 1: As-received powders have different phase composition. EOS powder is mostly austenite (γ) while LPW powder is mostly martensite (α').

As-built materials

Table 3 shows the oxygen and nitrogen content of the as-built specimens. As expected, the EOS material has substantially more N_2 than the LPW material. However, the gas atmosphere during processing does not have a significant effect. Nitrogen in the metal is not gained or lost significantly during SLM processing.

Table 3 shows Feritscope results for as-built specimens. The martensite content of the EOS material processed in N_2 is less than 4% for both processing atmospheres, i.e. it is almost completely austenite. Processing the EOS powder in argon has only a very small effect; the material is still more than 96% austenitic. The as-built LPW material is very different. It is at least 76% martensite in either process atmosphere, comparable to the commercial, condition A materials. As nitrogen is known to be an "austenite stabilizer" (Ulyanin, 1969), it is clear that the difference in as-built phase composition is due to the difference in nitrogen content of the powders.

Table 3. Element and phase composition for SLM processed materials.

Powder		EOS			LPW	
Build atmosphere		N_2		Ar	N_2	Ar
Layer (μm)		20	40	40	40	40
O (wt%)		-	0.04	0.04	0.08	0.07
N (wt%)		0.17	0.14	0.14	0.03	0.03
Feritscope martensite (%)	As-built	0.7	0.7	3.7	82	76
	650 °C heat treat	0.7	-	-	-	-
	788 °C heat treat	34	-	-	-	-

Figure 2 shows room temperature XRD patterns for specimens built (40 μm layer) from both powders using nitrogen and argon atmospheres. The R and L patterns are for the analysis plane perpendicular and parallel to the build plane, respectively. These as-built patterns are consistent with the Feritscope measurements. The LPW material is fully martensitic in all cases. The EOS material has some amount of austenite in both atmospheres, but more when built under N_2. The austenitic EOS material shows significant texture; the (111) reflection is very strong when the analysis plane is perpendicular to the build platform and very weak when the analysis plane is parallel to the build plane.

Optical and electron micrographs (Figure 3) of N_2 as-built EOS material show a unique microstructure. The optical micrograph shows the macrostructure typical of SLM processed material with overlapping, bowl-shaped features that result from solidification of the melt pool created by each laser scan. At higher magnification each of these features is seen to consist of very fine, parallel, cylindrical austenite grains. The average diameter of these is approximately 0.5 μm, while the length can be 40 μm or more, sometimes continuing across the boundary between two solidification features. This strong grain orientation is consistent with the observed XRD texture and indicates that solidification occurs with crystal growth perpendicular to the close-packed (111) austenite planes.

Effect of Heat Treatment

The Feritscope measurements (Table 3) for EOS material processed in N_2 show little conversion of the austenite for the 650°C heat treatment and very substantial conversion for the heat treatment at 788°C. High temperature XRD results provide additional understanding of the effect of heat treatment temperature. Figure 4 shows the intensity of austenite (111) and martensite (110) reflections for specimens mounted so that the analysis plane is parallel to the build plane. Because of strong preferred orientation, the austenite (111) reflection is weak. Heat treatment up to 700 °C has no effect on the phase composition either at high temperature or during cooling. When the heat treatment temperature is 750 or 800 °C, this reflection becomes substantially stronger and this "new" austenite transforms to martensite upon cooling. This change in behavior coincides with the α-γ transus temperature for iron (727 °C), the temperature at which ferrite transforms to austenite upon heating.

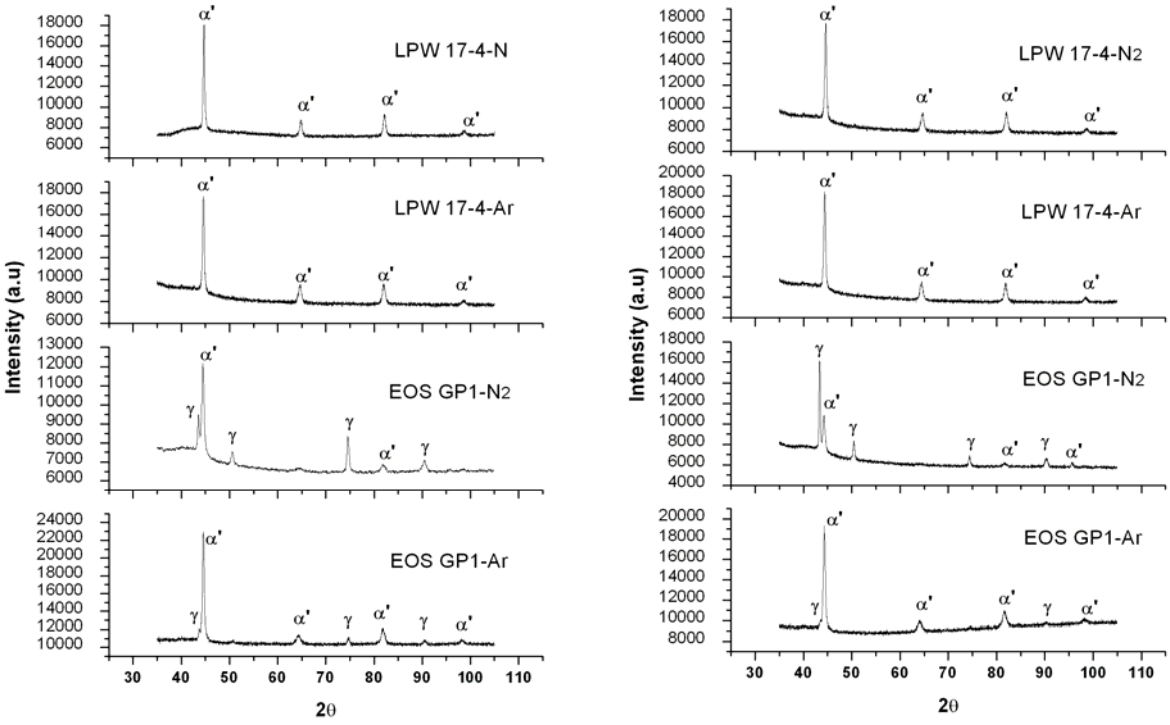

Figure 2: XRD patterns of as-built material are for the analysis plane perpendicular (R) and parallel (L) to the build plane. Consistent with Feritscope measurements LPW is mostly martensite (α') while EOS is shows significant austenite (γ).

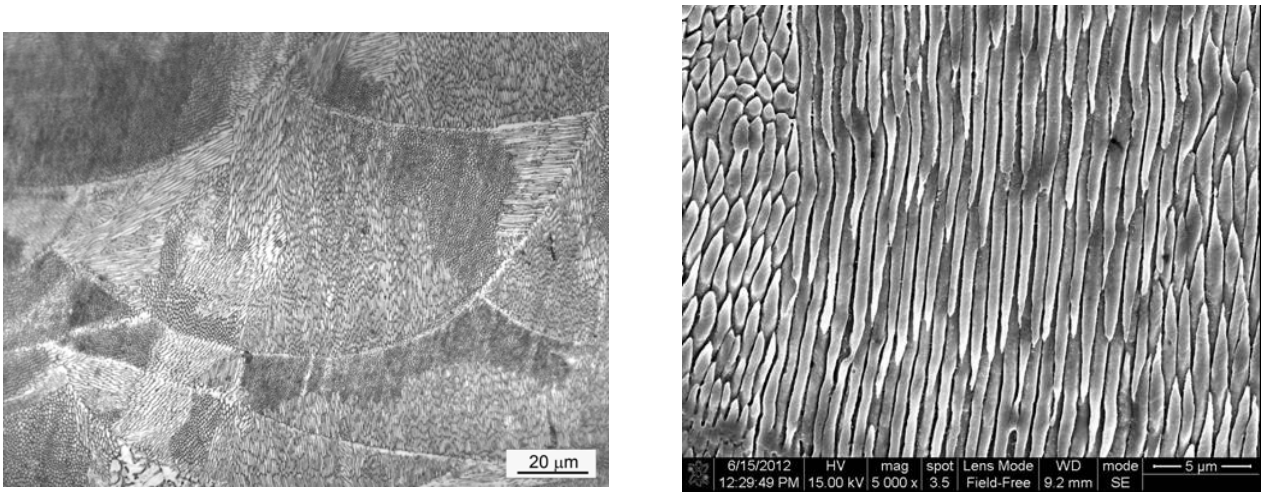

Figure 3. Optical (L) and scanning electron (R) micrographs show macrostructure typical for SLM process and strongly oriented, fine austenite grains.

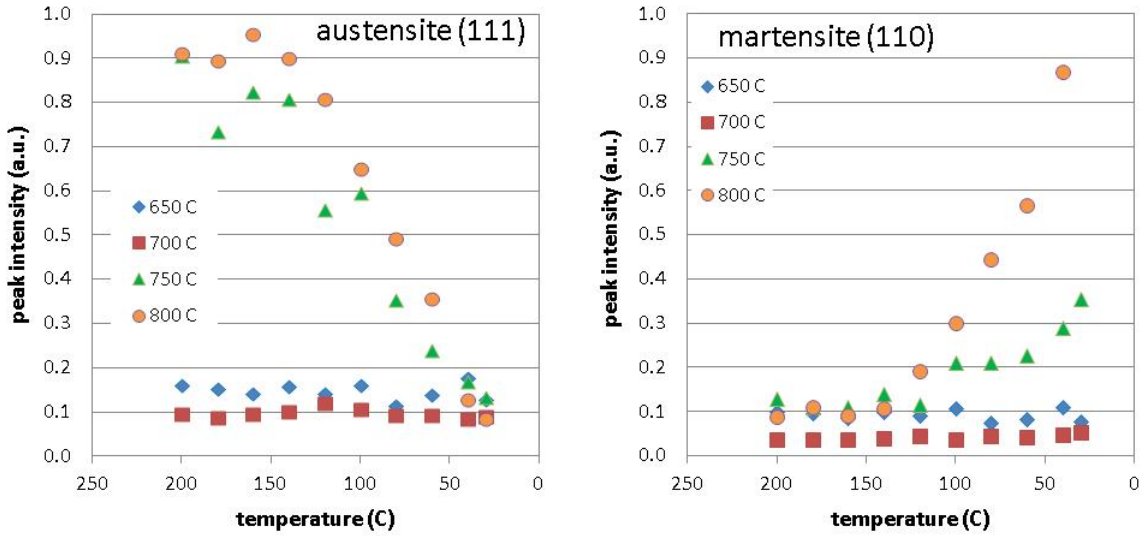

Figure 4. High temperature XRD of N_2-processed EOS material shows significant change in austenite characteristic at temperatures above 700 °C. This austenite transforms to martensite upon cooling to room temperature.

Mechanical properties

The metastable austenitic stainless steel created by SLM of high nitrogen 17-4 powder has interesting mechanical properties. Figure 6 shows the stress-strain curve for a tensile test of as-built EOS material using 20 µm layer thickness. The test specimen was built in the z-direction, i.e. the long axis is perpendicular to the build plane and parallel to the (111) planes of the oriented austenite grains. The elongation-to-fracture is almost 40%. Continuous Feritscope measurement during the tensile test shows that austenite starts to transform to martensite somewhat after reaching the yield point and continues until fracture. The final, plastically deformed material is 50% martensite.

The transformation from austenite to martensite also relieves residual stress in as-built material. Three rectangular parallelepipeds 5x5x50 mm were fabricated from the EOS powder under N_2. Residual thermal induced stress in the beams was measure by measuring distortion of the beams after release from the build plate. Table 4 shows the results for no heat treatment and for stress relief heat treatments at 650 °C (EOS-recommended) and 800 °C. The 650 °C temperature shows little change compated to no heat treatment. Raising the temperature to produce the phase transformation completely eliminates it.

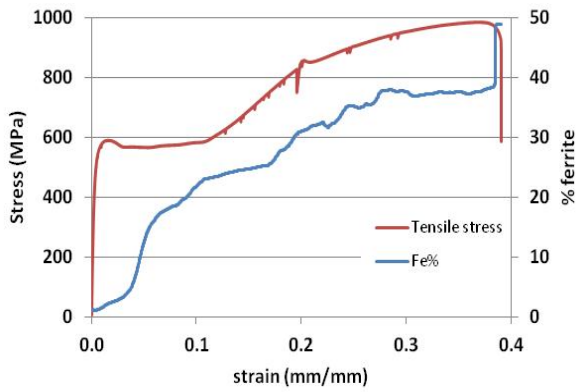

Figure 5. As-built EOS 17-4 stainless steel exhibits very large elongation to failure due to strain-induced transformation of the metastable austenite to martensite.

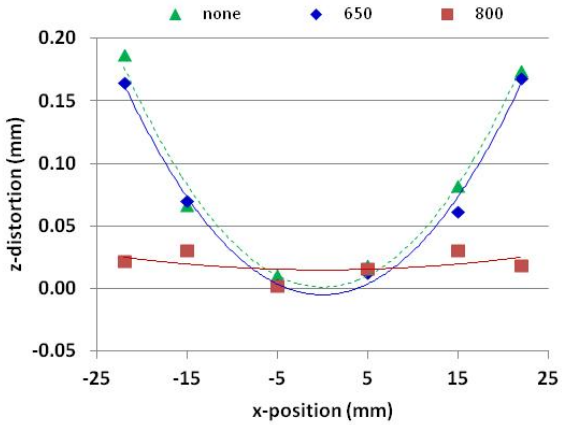

Figure 6. Stress relieving heat treatment is effective for temperature that produces the austenite-martensite phase transformation.

Conclusion

The combination of high nitrogen content and very fine, columnar grain structure yields an unusual metastable austenitic form of 17-4 stainless steel. The austenitic structure is stable up to the ferrite-austenite transus temperature. Heated above this temperature the material decomposes to the typical martensitic form upon cooling to room temperature. This occurs even though the nitrogen content of the metal has not changed. Thus, nitrogen content is not enough to explain the formation of stable austenite using EOS powder. The very fine, elongated grain structure also is needed to resist transformation to martensite during cooling.

The metastable austenite form of 17-4 stainless steel has certain unique and useful characteristics. Plastic deformation induces austenite to martensite transformation, resulting in a very large elongation prior to fracture. While this transformation-induced-plasticity (TRIP) has been observed in other steel alloys, it is not observed in 17-4 under normal processing methods. Also, transformation of the austenite by heat treatment above the transus temperature fully relieves residual stresses produced during the SLM process.

More generally, this study shows that microstructure and phase compositions produced by SLM of metal alloys can be very different than those produced by conventional manufacturing methods. Perhaps, with better understanding, these differences can be exploited to produce performance benefits unique to additive manufacturing methods.

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