NIST Technical Note 2006

Interlaboratory mechanical-property study for Cobalt-Chromium alloy made by laser powder-bed-fusion additive manufacturing

John A. Slotwinski William E. Luecke Eric A. Lass Antonio Possolo

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Interlaboratory mechanical-property study for Cobalt-Chromium alloy made by laser powder-bed-fusion additive manufacturing

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Abstract

An eight-laboratory study provided the data to evaluate variability in tensile mechanical properties of cobalt-chrome alloy (UNS R31538) made by metals-based additive manufacturing. In the study, six laboratories employed laser powder-bed-fusion additive manufacturing, and two additional laboratories employed electron-beam powder-bed fusion. For the five laboratories that employed nominally identical laser powder-bed fusion systems, the between-laboratory variability in yield strength and tensile strength was several times larger than the within-laboratory variability. Microstructural analysis using scanning electron microscopy revealed that each laboratory produced slightly different microstructures. Thermodynamic modeling of the solidification and subsequent post-build heat treating demonstrated that the final microstructure is sensitive to the exact heat-treating conditions.

Key words

additive manufacturing; ASTM F75; laser-powder-bed fusion; yield strength.

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1. Introduction

Recently, the visibility of metals-based additive manufacturing (AM) has significantly increased. It has achieved impressive niche successes, such as a metal jaw replacement [1] and the announcement of plans to produce metal fuel nozzles for aerospace engines [2]. This vision for metals-based additive manufacturing is simultaneously imaginative, outrageous, and inspiring. And while it is difficult to accurately predict the full impact of metals-based additive manufacturing, it is easy to see how it could potentially affect the aerospace, defense, medicine, and transportation industries. However, before the vision of metals-based AM can be realized, significant technical challenges must be overcome [3, 4].

Several of these challenges are related to metals-based additive manufacturing materials. Specifically [3][4]:

- 1. Understanding of the dependence of material properties on powder properties and process parameters is limited.
- Standardized methods for qualifying and certifying AM parts and AM materials do not exist.
- 3. Traditional methods for material qualification for AM materials are largely impractical in time, effort, and cost [5].
- 4. AM material data, both general data, and high-quality, pedigreed, traceable data that is necessary for design-allowable databases, are lacking.
- 5. No standardized AM-specific methods for conducting AM material interlaboratory studies exist [6].

To address these challenges, NIST coordinated a materials interlaboratory study ("round robin") to assess the variability in the mechanical properties of additively manufactured cobalt chrome (CoCr UNS R31538) tensile bars. This material was selected because of its potential use as bio-medical implants and because its associated process parameters for AM powder bed fusion systems is already known for some commercial systems. The goal of the study was not to assess specific materials or processes per se, but rather to help develop the test protocols and analysis methods that will be used in future, more extensive round robins that lead to the certification of AM materials and the development of design-allowable databases. In addition, NIST employed statistical engineering expertise to examine these results to determine what the minimum number of participants and minimum number of specimens was needed for a round robin study of this type to have meaningful results.

2. Experimental Methods

This report strives to comply with the requirements of ASTM F2971-13[7]: "Standard Practice for Reporting Data for Test Specimens Prepared by Additive Manufacturing," ex-

Parameter	Core	Skin	
Scan Pattern	Checkerboard	Striped	
Feature Size	8 mm wide squares	4 mm wide stripes	
Laser Power	195	W	
Scan Speed	800 mm/s		
Layer Thickness	$20 \ \mu m$		
Atmosphere	N_2		
Raster Line Separation	0.10 mm		

 Table 1. Nominal build parameters for test specimens in laboratories 1 through 5.

cept that certain identifying features of the laboratories are omitted as part of the confidentiality of the interlaboratory study process.

2.1 Additive manufacturing

The focus of the study was on five nominally identical commercial laser powder-bed fusion systems with 200 W lasers that used nominally identical parameters shown in Table 1. The other laboratories included one that used a powder-bed-fusion system with a 400 W laser, and two that used commercial electron-beam powder-bed-fusion systems. All aspects of the round robin were kept as consistent as possible for each of the participants. Laboratories 1 to 5 used laser powder-bed-fusion systems and nominally identical, virgin square build platforms, made from 1045 steel 25.4 mm thick, and 250 mm wide. The other participant used a similar build platform approximately 50 mm thick. The electron-beam powder-bed-fusion systems did not require a build platform. Seven laboratories built the specimens with the T dimensions (Figure 1) parallel to the normal to the plane of the build platform (the Z-axis as defined in ISO/ASTM 52921:2013(E) [8], and with the long axis of the specimen parallel to the recoating direction, which is the usual X-axis as defined in ISO/ASTM 52921:2013(E). The orientation of these specimens is designated XYZ in the orthogonal orientation notation system of ISO/ASTM 52921:2013(E). Laboratory 7 built the specimens with the C dimension in Figure 1 parallel to the Z-axis, i.e. this specimen is designated XZY orientation. All participants used virgin CoCr powder from the same production heat, except that one electron-beam system participant used its own commercially available powder. Each participant received 20 kg of powder, supplied in two 10-kg containers. Before distribution each container was sampled using good industry practice [9] and tested for consistency [10]. Table 2 summarizes the chemical composition of the powder, taken from a report supplied by the manufacturer. Table 3 summarizes some size characteristics of the powder, previously reported [11].

No powder characterization results indicated any significant differences in the density, particle-size distribution, or particle aspect ratio of the powder in the individual 10-kg containers.

Table 2.	Chemical	analysis of	the	powder,	reported	by	the	manufacturer
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Element	Co	Cr	Mo	Si	Mn	Fe	С
Mass fraction %	62.4	28.6	5.9	0.8	0.7	0.09	0.15

Notes:

- Ni, W, Ti Al: all < 0.1 % mass fraction
- S, B, Be, Cd: all < 0.01 % mass fraction
- P: 0.01 % mass fraction
- C and S determined by combustion. All other elements determined by inductively coupled plasma mass spectrometry (ICPMS)

Table 3. Characteristics of the powder supplied to the participants.

Characteristic	Method	Parameter	Value	Source
Density	He pycnometry	ρ	(8.3 ± 0.01) g/cm ³	[11]
Particle size distribution	laser diffraction	<i>D</i> (0.1)	$(8.93\pm0.40)\mu\text{m}$	[11]
	laser diffraction	<i>D</i> (0.5)	$(23.04\pm0.96)\mu\text{m}$	[11]
	laser diffraction	<i>D</i> (0.9)	$(44.69 \pm 1.54) \mu m$	[11]
	sieve analysis	>45 µm	3 %	MTR
	sieve analysis	>63 µm	0.5 %	MTR
Phases	x-ray diffraction		primarily FCC	[12]
Particle shape	x-ray computed tomography and scanning- electron microscopy		nominally equiaxed	[11]
Notes:				

• D(X): fraction of the particles with diameter less than D.

• MTR: manufacturer's test report, dated 04.08.2011

• FCC: face-centered cubic crystal structure.

After fabrication, the participants returned the build platforms with the tensile specimens still attached. Before the specimens were removed, the entire build platform with the specimens was heat treated in a stainless steel bag surrounded by flowing argon by heating to 1050 °C over about 7 hours, holding for 1 hour and then cooling in the furnace after the furnace power was shut off. The specimens from one of the electron-beam powder-bed-fusion system (laboratory 7) were not heat treated. After heat treating, the specimens were removed from the build platforms by electrical discharge machining (EDM). The surfaces of the specimens were not machined after removal, and were left in the as-built or EDMed condition.

2.2 Post-fabrication Characterization

One tested specimen from each laboratory was characterized by scanning electron microscopy to understand the relation between the mechanical properties and the microstructure. Specimens came from the center of the nominally undeformed head of the specimen, which was sectioned and metallographically polished, but not etched. Images were acquired by driving the microscope stage to a random position along the center line of the specimen, ensuring that no preparation artifacts existed in the field of view, and then acquiring images. Both back-scattered electron images, which are sensitive to atomic number variation, and secondary-electron images, which are sensitive to topography as well as energy-dispersive x-ray spectroscopy (EDS) maps were acquired.

2.3 Tensile testing

Each laboratory produced eight specimens, and of which seven were tested, except Laboratory 1 (eight specimens) and Laboratories 2 and 3 (six specimens). An accredited private testing laboratory determined the mechanical properties of all specimens in accord with ASTM E8/E8M [13], which is cited in the corresponding "ASTM Standard Guide for Evaluating Mechanical Properties Made by Additive Manufacturing Processes" [14]. Figure 1 shows the test specimen and the actual dimensions produced by the eight laboratories. The 0.20 % offset yield strength was determined in strain control from the extensometer at a strain rate de/dt = 0.016 (mm/mm)min⁻¹. After yield was determined, the extensometer was removed at $e \approx 0.009$, and the tests continued to failure in displacement control at a rate that produced a nominal engineering strain rate = 0.05 (mm/mm)min⁻¹.

3. Results

3.1 Tensile stress-strain curves

Figure 2 shows the tensile stress-strain curves for all the test specimens. The stress-strain curves fall into two groups, which correspond to the two different process methods. Table 4 and Figure 3 summarize the mechanical properties results. Figure 3 uses box plots: each rectangular box comprises the middlemost 50 % of the data, and the whiskers, if present,

 Table 4. Tensile mechanical property data for all tested specimens.

Lab	Parameter	Values
1	$S_y(MPa)$	828 843 830 819 827 838 825 833
1	$S_u(MPa)$	1230 1209 1211 1210 1223 1197 1235 1211
1	$El_t(\%)$	11 9 8 9 10 8 11 6
2	$S_y(MPa)$	944 929 930 928 929 934
2	$S_u(MPa)$	1270 1262 1239 1269 1262 1271
2	$El_t(\%)$	665646
3	$S_y(MPa)$	878 871 880 896 863 892
3	$S_u(MPa)$	1211 1209 1205 1209 1220 1220
3	$El_t(\%)$	565656
4	$S_y(MPa)$	895 893 894 889 880 876 878
4	$S_u(MPa)$	1201 1177 1196 1188 1190 1200 1191
4	$El_t(\%)$	5 3 5 5 5 5 5
5	S_y (MPa)	917 928 937 916 927 920 912
5	$S_u(MPa)$	1176 1193 1211 1183 1143 1125 1187
5	$El_t(\%)$	2112112
6	S_y (MPa)	841 858 838 852 849 844 853
6	$S_u(MPa)$	931 962 981 973 1020 971 1007
6	$El_t(\%)$	1 0 1 2 2 0 1
7	$S_y(MPa)$	635 607 609 605 585 605 634
7	$S_u(MPa)$	738 675 737 727 706 738 729
7	$El_t(\%)$	3 5 3 3 3 3 2
8	$S_y(MPa)$	614 635 621 620 627 624 613
8	$S_u(MPa)$	738 781 754 744 756 706 747
8	$El_t(\%)$	3 3 3 1 1 1 2

Notes

- S_y : 0.2 % offset yield strength
- S_u : tensile strength
- *El*_{*t*}: elongation in 25.4 mm
- Values are listed in specimen order for all parameters



Fig. 1. Tensile specimen. Upper right corner shows nominal width and thickness dimensions for each laboratory.

extend to the extreme data points. The thick, horizontal line drawn inside the box marks the location of the median. The reported yield strength is the 0.2 % offset yield strength, and the elongation is measured over a gauge length, G=25.4 mm. For yield strength, and considering only laboratories 1-5, the between-laboratory standard deviation is about five times larger than the within-laboratory variability, suggesting substantial heterogeneity between laboratories. None of the specimens necked before failure. Note that specimens from Laboratory 6 failed shortly after yield at small elongation at the end rather than within the gauge length. These failures at very small strains of the laboratory 6 specimens resulted in large part for their lower average tensile strengths.

4. Discussion

4.1 Mechanical Properties

The statistical model for the value $x_{i,j}$ of each of the four measurands (tensile strength, yield strength, elongation, and elastic modulus) measured on test specimen *i* produced by laboratory *j* expresses itself as an additive superposition of three different effects:

$$x_{i,j} = \mu + b_j + e_{i,j} \tag{1}$$

Toman and Possolo [15, 16] call this expression a laboratory (random) effects model. Here, μ denotes the true value of the parameter, e.g. tensile strength, for this material that results from this manufacturing process. The term b_j is the effect of laboratory j, and $e_{i,j}$ is the effect of the particular test specimen. The index j includes $j = 1, ..., n_L$, where n_L denotes the number of laboratories The index i includes $i = 1, ..., n_j$, where n_j denotes



Fig. 2. Tensile stress-strain curves. The maximum strain corresponds to removal of the extensioneter and not to specimen failure.





Fig. 3. Box plots of measurement results from all laboratories. Those painted blue were used in the statistical analyses described in Section 4.1.

MEASURAND	Symbol	$\widehat{ au}/\widehat{\mu}$	$\widehat{\tau}/\operatorname{median}(\{\widehat{\sigma}_j\})$
		%	ratio
tensile strength	S_u	2.6	2.7
yield strength	S_y	4.5	4.9
Elongation $G = 25.4 \text{ mm}$	El_t	51	3.5
Elastic modulus	E	2.1	0.5
	Notes:		

Table 5. Evaluation of between-laboratory differences derived from fitting laboratory (random) effects models to the values measured by laboratories 1 to 5.

• $\hat{\tau}/\hat{\mu}$: between-laboratory variability, $\hat{\tau}$ normalized to the mean value, $\hat{\mu}$.

the number of test specimens from laboratory j. For this study $n_L = 5$, and with $n_j = 7$, for most laboratories. Furthermore, the $\{b_j\}$ are modeled as (non-observable) outcomes of independent, Gaussian random variables with mean 0 and standard deviation τ , which characterizes the between-laboratory dispersion of values. The $\{e_{i,j}\}$ are modeled as (non-observable) outcomes of independent, Gaussian random variables with mean 0 and standard deviation σ_j , which characterizes the dispersion of values within laboratory j, and may vary between laboratories.

These models were fitted using function lme of package nlme [17] for the R environment for statistical computing and graphics [18]. Their adequacy to the data was evaluated by graphically examining the corresponding estimates of the laboratory and test specimen effects.

Table 5 summarizes the results that may be relevant to the design of future, more ambitious interlaboratory studies of metals-based additive manufacturing. The between-laboratory dispersion of values, expressed relative to the estimate of the measurand, listed in the column labeled $\hat{\tau}/\hat{\mu}$ (%), is modest (2 % to 5 %) except for elongation, for which the between-laboratory variability is surprisingly large. The between-laboratory variability is three to five times larger than the typical within-laboratory variability, listed in the column labeled $\hat{\tau}/\text{median}(\{\hat{\sigma}_j\})$, for all measurands except the elastic modulus. The fact that the between-laboratory variability (τ) is substantially larger than the within-laboratory variability is common in inter-laboratory studies involving a technology still poorly understood or in development.

An important conclusion from Figure 3 and Table 5 is comes from the large ratio of between-laboratory variability to within-laboratory variability. Potential differences in parent material, combined with unknown processing differences, induce large differences in material properties. These material-property differences occurred despite the fact that the processes in laboratories 1 through 5 were nominally identical, and all five laboratories started with powder with the same measured nominal characteristics from the same batch. The reproducibility of properties of the same product, between manufacturers operating independently of one another, is generally regarded as a sign of a mature technology. Generally this means that the differences in the values of those properties between manufacturers should be similar to the variability of the values observed among units manufactured by the same producer. This interlaboratory study revealed that this is not quite the situation yet in this additive manufacturing experiment. In fact, the last column of Table 5 shows that differences between laboratories, even between those that have used the very same parent material and manufacturing process (the only ones considered in the analyses that produced the results summarized in this table), are considerably more important than differences between test specimens manufactured in the same laboratory. For yield strength, for example, the variability component attributable to differences between laboratories is 4.9 times larger than the variability component attributable to differences between test specimens manufactured by the same laboratory.

An important output of our analysis is an estimate of the interlaboratory variability τ . Since differences between laboratories is the largest source of variability of the results, it is important to characterize it accurately, in particular to be able to detect collective improvement (meaning better reproducibility) in the community of users. For this purpose, increasing the number of participating laboratories appears to be a more compelling need than increasing the number of test specimens manufactured by each laboratory. In addition, increasing the number of laboratories also reduces the uncertainty associated with the consensus value that summarizes all the measurement results. For yield strength, for example, increasing the number of participating laboratories four-fold brings about gains in precision that are comparable to those resulting from quadrupling the number of test specimens manufactured by each laboratory.

4.1.1 Expected variability in mechanical properties

The mechanical properties literature has many characterizations of the variability of mechanical properties of specific engineering alloys. The data from these studies are the basis for estimating the reliability of metal components. Unfortunately, no formal multilaboratory intercomparison of mechanical properties made by metals-based additive manufacturing exists for comparison to this study.

Figure 4 compares the data of this study to other analyses of the expected variability of mature engineering structural alloys. The rightmost panel, labeled "Builds" is the coefficient of variation of the yield strength produced by the builds of Laboratories 1 through 6, which used the laser powder-bed-fusion method. The coefficient of variation, V_r is defined as the ratio of the standard deviation to the mean yield strength:

$$V_r = \frac{\mathrm{sd}(S_y)}{\bar{S}_y} \tag{2}$$

The panel second from the right, labeled "Overall" is the coefficient of variation of the entire set of n = 41 tensile tests from laboratories laboratories 1 to 6, which used laser powder-bed fusion.

Fig. 4. Coefficients of variation of the yield strength for this study compared to other literature data. The dashed line shows the average value, $\overline{V_r}$, of the data in each panel.

The remaining four panels in Figure 4 present four different types of variability of yield strength, presented also in a previous report [19].

E8 within-lab The data in the first panel come from a study [20] that established the precision and bias of ASTM E8/E8M [13], the standard method for conducting a tensile test to establish strength of metals. Each data point represents the coefficient of variation of a single alloy tested in one laboratory on a single day. This coefficient of variation represents the minimum that is achievable for any engineering alloy.

E8 between-lab The data in the second panel, from the same study [20], include the variation of the same alloys but now tested in multiple laboratories. The increased in variability represents mostly the differences in each laboratory's realization of the E8/E8M [13] method.

Structural steel The data in the third panel come from four structural steel industry studies [21–24] to establish the variability in the mechanical properties of steel used in building construction. The data originate primarily from hot-rolled shapes. These variability estimates find their way into estimates of the factors of safety in construction. The steels were supplied to many different standards and grades, but each has a minimum specified yield strength, so the distribution of strengths may be truncated at low strength. Each data point represents a specific steel standard or grade within a standard, usually including steels from different mills and sometimes made by different processes.

Wrought alloy The fourth panel contains two data sets on wrought structural alloys. One is from a study [25] of four Swedish pressure-vessel steels made in different steel mills. The other data set comes from from the Metallic Materials Properties Development and Standardization Handbook (MMPDS) [26], which is the authoritative source of designallowable mechanical-properties data for the aerospace industry. In this set, each data point represents an individual alloy in a given heat and orientation. The coefficients of variation are based on experimental data from multiple heats and mills, critically evaluated by industry experts.

Comparison to this study The sizes of coefficients of variation for the individual builds are similar to the E8 within-lab measurements, which shows that the level of homogeneity of an individual build is comparable to a mature engineering alloy, and that the tensile tests were conducted properly. The overall coefficient of variation is about four times larger than that for the individual builds. Its size is similar to the coefficients of variation from mature engineering alloys produced in different mills, by different processes. This large variability arose despite efforts to control the starting powder, machine, and build conditions. None of these parameters were controlled in the the structural steel [21–24] and wrought alloy studies [25, 26]. Indeed, in those two studies, all of those parameters were deliberately varied to estimate the expected variability in commercial products.

Fig. 5. Representative micrograph (Lab 3) illustrating the microstructural features of the additively manufactured Co-Cr-Mo alloys. Backscatter electron SEM image. Build direction is horizontal.

4.2 Microstructural Analysis

The mechanical properties of the specimens from the five laboratories that used nominally identical processes are not identical. The differences could arise if unmonitored process differences during metals-based additive manufacturing or subtle differences in the postbuild heat treatment produced materials with different microstructures. Figure 5 presents a backscatter electron (BSE) SEM image of a representative sample of the microstructure found in the metals-based additive manufactured Co-Cr-Mo alloy. The BSE image is sensitive to atomic number (the brighter the phase the higher the atomic number), and thus provides some information on the phase composition, as well as phase contrast. Grain interiors looks to be comprised primarily of a single matrix phase. Several secondary phases are observed as well, including intergranular bright (higher average atomic number) and dark (lower average atomic number) precipitates hundreds of nanometers in size decorating grain boundaries and very fine-scale bright intragranular precipitates only a few tens of nanometers in size within the grains, often observed in linear arrays depending on the orientation of the grain intersecting the sample surface. The darker precipitates may be lean in the heavier element Mo compared to the matrix, or enriched in the lighter elements C and/or Si; while the bright precipitates must enriched in Mo the low amount of C and Si in the bulk means that the average atomic number cannot significantly increase by removing it.

Figure 6 presents an x-ray diffraction (XRD) pattern for a laser-powder-bed-fusion produced CoCrMo sample after post-build heat treatment. The pattern indicates the presence of three phases, HCP, FCC, and a small amount of $M_{23}C_6$ carbide. The presence of HCP is unexpected since conventionally cast CoCrMo is expected to consist of an FCC matrix with secondary phases of σ -phase and carbides of various forms depending on exact composition and processing history [27, 28]. However, HCP, formed martensitically from the FCC phase upon cooling from elevated temperatures, has been reported in CoCrMo alloys, albeit in volume fractions of only about 5 %[29]. From Figure 6, HCP is more prevalent than FCC. Because the martensitic transformation to HCP from FCC results in identical compositions for the two phases, and the matrix in Figure 5 appears as a single phase even though it actually contains both FCC and HCP. The presence of an HCP instead of a fully FCC matrix would explain the increased strength and reduced ductility of the metals-based additive manufactured CoCrMo alloys compare to ASTM F75.

Figure 7 presents an elemental map and corresponding SEM image constructed using energy dispersive x-ray spectroscopy (EDS). The dark precipitates are enriched in C, while the bright precipitates are enriched in Mo, consistent with the secondar electron image, and also in Si. Because the dark precipitates do not appear to the deficient in Mo, the decrease in average atomic numberis most likely because they are rich in C, which cannot be detected reliably using SEM/EDS. The dark precipitates are therefore identified as $M_{23}C_6$ carbides. The bright Mo- and Si-rich precipitates cannot be positively identified using the combined results of XRD and SEM/EDS.

The Thermocalc software package[29] was used in conjunction with the Thermocalc TCNI6 Ni-based alloy database [30] to perform thermodynamic calculations for the CoCrMo alloy to further understand the observed microstructures. The alloy composition presented in Table 2 was used in the calculations, neglecting elements with mass fraction less than 1 % except Si and C. Figure 8a presents a Scheil simulation showing the solidification pathway as the alloy cools from the liquid phase. The first phase to form from liquid is FCC. When solidification reaches about 85 % complete, BCC phase begins to form. Finally, as the last few percent of liquid solidify, two carbide phases, $M_{23}C_6$ and M_2C in Figure 8a), form as well. The predicted solidified microstructure contains 91 % (by mole fraction) of FCC phase, 8 % of BCC phase, about 1 % $M_{23}C_6$, and a minute fraction of M_2C . Figure 8b shows that the liquid phase becomes enriched with Mo and Si as solidification proceeds, and the final drops of liquid to freeze may have mass fractions as high as 0.25 and 0.04, respectively. These fractions are several times that of the powder feedstock. The last liquid to solidify produces the interdendritic regions of the solidification microstructure, and correspond to the arrays of fine-scale intragranular Mo-rich precipitates in Figure 5. The

Fig. 6. XRD pattern of additively manufactured CoCrMo alloy after post-build heat treatment.

(e) Si

Fig. 7. SEM image (secondary electron image) and corresponding EDS map confirming that the dark precipitates are rich in Cr and the bright precipitates are rich in Mo and Si. Build direction is horizontal. Scale bar is the same in all images.

Fig. 8. a) Scheil simulation showing mole fraction of each phase present as solidification proceeds for a CoCrMoSiC alloy. b) The calculated liquid composition as a function of solidified fraction. c) Calculated isopleth phase diagram as a function of Mo-concentration for constant Cr, Si, and C. d) Calculated isopleth phase diagram as a function of Si-concentration for constant Cr, Si, and C.

spacing of the interdendritic regions give a relative measure of solidification rate. The faster solidification occurs, the more closely space the dendrites become (compare Figure 9 for laser-produced material to Figure 10 produced using electron beam systems).

The Scheil simulation reasonably predicts the presence of the FCC matrix, although a large fraction of FCC has transformed to HCP upon cooling, and the dark $M_{23}C_6$ precipitates observed in the specimens. However, in traditionally cast CoCrMo alloys experiments [27, 28] demonstrate that the σ -phase occurs instead of BCC, and several other carbides form, including M7C3 and M6C, instead of M2C. Figures 8c and 8d present two sections of the CoCrMoSiC phase diagram: one as a function of mass fraction Mo and the other as a function of mass fraction Si. Both indicate that at the temperature of the postbuild heat treatment, σ -phase is an equilibrium phase. The bright precipitates in Figure 5 are most likely this σ -phase; which may have formed during solidification, as observed in conventionally cast CoCrMo, or during the post-build stress-relief heat treatment. The observed volume fraction of the secondary phases may vary from those calculated from the thermodynamic modeling, either as a result of uncertainty in the model or because of the enriched regions of Mo and Si that arise from the solidification process. Figure 8c and 8d illustrate that the increased Mo and Si concentrations can cause an increase in the fraction of secondary phases (observed locally), or in extreme cases introduce entirely new phases not expected in the conventional produced alloys, including R-phase, a ternary Co-Cr-Mo phase, and C14 Laves phase.

Representative micrographs of the material from each laboratory using laser-powderbed fusion systems are presented in Figure 9 (Labs 1 through 6), grouped by relative strength. In the sample from Lab 6, the rows of intragranular bright, Mo-rich precipitates are coarser than those in the five other labs using laser-powder-bed processing. This coarsening is likely due to the increased power of the laser used by Lab 6 (400 W versus 200 W) compared to other labs which increases the heat input and ultimately the cooling rate during the building process. The coarser precipitates also likely contributes to the relatively low strength of the Lab 6 material, compared to the other laser-produced materials, with the exception of Lab 1.

Figure 10 shows representative micrographs of the two electron-beam powder-bedfusion produced specimens from Lab 7 and Lab 8. The bright, intragranular precipitates in both samples are significantly larger than those in the laser powder-bed-fusion-produced materials, a result of the higher energy input from the electron-beam, preheated chamber, and slower cooling rate. The decreased strength of electron-beam produced specimens relative to the laser-produced ones is a result of this coarser microstructure and larger secondary phase precipitates. The specimen from Lab 7, which did not undergo a post-build heat treatment, has regions of a eutectic solidification structure that include at least three phases. Based on the contrast in the image, these phases are probably FCC, $M_{23}C_6$, and a third phase that is more enriched in Mo than the bright precipitates found in the other specimens. These regions also occur as a result of the slower cooling in the electron-beam process compared to laser process. Remnants of this structure can be seen in the other electron-beam produced sample, Lab 8.

(a) High Strength: Lab 2 S_y=932 MPa

(b) High Strength: Lab 5 S_y=923 MPa

(c) Medium Strength: Lab 3 S_y =880 MPa

(d) Medium Strength: Lab 4 S_y =886 MPa

(e) Low Strength: Lab 1 S_y =831 MPa

(f) Low Strength: Lab 6 S_y=848 MPa

Fig. 9. Representative BSE images of the microstructure of specimens from laboratories that use laser-powder-bed fusion systems, grouped by yield strength. Build direction is horizontal.

(c) Low magnification: Lab 8 Sy=738 MPa

(d) High magnification: Lab 8 S_y =738 MPa

Fig. 10. Representative BSE images of the microstructure of specimens from the two laboratories that use electron-beam-powder-bed fusion systems. Build direction is vertical for Lab 7 and horizontal for Lab 8.

Т	mass fraction C	mole fraction FCC	mole fraction σ	mole fraction M ₂₃ C ₆
°C	%	%	%	%
1025	0.15	89.2	8.0	2.8
1050	0.15	91.4	5.9	2.7
1075	0.15	93.3	3.8	2.6
1050	0.05	90.7	7.6	1.7
1050	0.15	91.4	5.9	2.7
1050	0.25	92.1	4.2	3.7

Table 6. Equilibrium mole fractions of the three equilibrium phases FCC, σ , and M₂₃C₆, for Co-Cr-Mo-Si-C alloys containing the same mass fractions of Cr, Mo, and Si, 28.6 %, 5.9 %, and 0.8 %, respectively, with different C contents and at different post-build heat treating temperatures.

Both the mechanical properties and microstructures of the specimens from the different laboratories that used nominally identical processes are not identical. The differences could arise as a result of unmonitored process differences during additive manufacturing or subtle differences in the post-fabrication heat treatment. Table 6 demonstrates that the equilibrium amount of σ -phase, calculated using Thermocalc, may vary quite substantially with temperature. The equilibrium volume fraction of σ at the target annealing temperature is 5.9 %, but can vary from 3.8 % to 8.0 % if the temperature decreased or increased, respectively, by 25 °C. Changes in temperature will also affect kinetics and coarsening rates, as well as the FCC to HCP martensitic transformation observed in the additively-produced CoCrMo specimens. A higher temperature may allow a more rapid evolution toward equilibrium and result in a coarser microstructure with larger σ and M₂₃C₆ precipitates. Conversely, a specimen annealed at slightly lower temperature may display much finer precipitate phases. Table 6 also illustrates that variations in composition may have a noticeable effect on final microstructure. Increasing the amount of C significantly decreases the equilibrium fraction of σ -phase and increases the fraction of M₂₃C₆ and vice-versa for a decrease in C-content. Carbon contamination may readily occur during routine handling of the powder, e.g. adsorbed organic materials on the powder surface or build chamber walls that decompose when heated during the building process, and most likely is unmonitored once the powder is received. Nitrogen behaves very similarly to carbon, substituting for it in carbides to form carbonitride phases with the same crystal structures as their carbide counterparts., Nitrogen is easily picked up by the material either during powder atomization, which is often conducted using nitrogen gas, or during the building process itself, where nitrogen gas was used as a protective atmosphere. From the Thermocalc calculations, adding a mass fraction of 0.1 % N reduces the equilibrium volume fraction of σ to 4.5 %, and also introduces a fourth phase. In addition to 2.7 % M₂₃C₆, 1.4 % M₂(C,N) is also predicted to form, which is the same phase as predicted by the Scheil simulation, Figure 8a with N substituting for C forming a carbonitride. Nitrogen may also affect the FCC to HCP martensite transformation similarly to its effect on the FCC to martensite transition in Fe-based alloys. A more detailed investigation of the effects of composition, processing parameters, and post-processing is required to understand how the final microstructure arises and how it affects the properties of the resulting material.

Figure 9 shows that the relative strength of the material correlates with the size and distribution of the secondary phases. A higher volume fraction of secondary phases and larger average precipitate size results in a material with lower strength, evidenced by the microstructures of Lab 1 and 6. The possible exception to this observation is Lab 5, though the secondary phase fraction is noticeably less than that found in Lab 1 or 6, and looks to be slightly less than that of Labs 3 and 4. Again, the increased strength of the additively produced material, yield strengths of about 830 MPa to 930 MPa, and decreased ductility, about 1 % to 5 % strain to failure for five of the six labs, compared to that expected of ASTM F75 [31]($S_y \ge 450$ MPa and elongation ≥ 8 % on a 2-inch gauge length) is likely a result the high fraction of HCP in the microstructure.

5. Conclusions

- The large ratio of between-laboratory variability to within-laboratory variability in mechanical properties, typically about 3, is consistent with a new rather than mature production technology. (Table 5)
- The variability in mechanical properties measured in this study is comparable to the accepted variability in mature engineering alloys made by multiple mills and processes at different times, despite the much closer control over starting materials and process. (Figure 4)
- This study highlights that even nominally identical processes can introduce significant variability into the mechanical properties of alloy specimens made by metalsbased additive manufacturing. (Figure 2)
- Future interlaboratory studies should employ more than five laboratories, but five or six specimens per laboratory is probably sufficient. (Section 4.1)
- The microstructures that result from the post-build heat treatment are sensitive to the carbon content and temperature of the heat treatment. (Figure 8 and Section 4.2).

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The order of the list above is random, and does not correspond to the numerical laboratory identifiers.

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Appendix A: Supplemental Materials

The data plotted in Figure 2, Figure 3, Figure 6, and Table 4 are available in digital form at DOI:10.18434/T4/1502566 https://dx.doi.org/10.18434/T4/1502566.