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On the Benefits of High Pressure Heat Treatment in Additively Manufactured CoCr

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Abstract

Laser Powder Bed Fusion (L-PBF) processes are becoming more viable in place of traditional castings in a variety of industries. To compete, novel material grades are being considered with additive manufacturing (AM). In maximizing performance and manufacturing efficiency through AM, a novel approach to heat treatment and Hot Isostatic Pressing (HIP) processing needs to be considered. It has been shown that combining key heat treatment processes with (HIP) by utilizing fast cooling rates can benefit static properties as well as improve turn-around time for HIP processing [1,2]. Argon pressures up to 207 MPa with cooling rates above 170°C per minute are now available in production sized HIP systems to design ideal HIP cycles for high pressure heat treatment. Additive manufacturing with high pressure heat treatment is in need of further investigation for establishing new qualification standards. This study investigates designed High-Pressure Heat Treatment cycles to consider mechanical performance on LPBF CoCr. The combined cycles investigate possible alternatives to historically accepted two step HIP then heat treat processing by combining densification with homogenization treatment into one step. Tensile, fatigue, hardness, microstructure and Charpy impact performance are explored to seek optimal properties and with streamlined thermal processing. It was found that all trial conditions exceeded Electron Beam Melted (EBM) AM CoCr expectation, but traditional processing provided a slight advantage in ultimate tensile stress. One of the novel processes explored, "common" was found to provide a slight improvement on yield stress and direct hardness. Published fatigue data is rare for CoCr, however data generated from this study showed a slight advantage to the "common" HPHT process primarily for lower applied stress levels. Microstructures were comparable across all trial processes. It is recommended that each novel processing route be considered as viable alternatives to traditional processing, but that the "common" processing may prove advantageous for both mechanical properties and streamlined manufacturing.

Introduction

Industry Background

L-PBF continues to transition to production. Adaptations of established manufacturing methods and materials are required to consider the shift. The bar of success is placed to meet or exceed the property performance of traditional design approach such as castings or a wrought and fabricated part. Aside from new efficiency gains from flexible design advantage, material properties need to stay competitive. Additionally, the time to manufacture is being brought to a new level through additive manufacturing. Streamlined production is crucial to the value proposition of laser based AM. All levels of the process stream need to be considered in optimizing production AM [1,2].

Cobalt Chrome alloys have been adapted to a variety of industries due to their rounded excellence for corrosion resistance, good wear resistance, and modest strength [3]. CoCr F75 is a cast grade traditionally utilized for medical implants. CoCr F75 is amply suited for knee and shoulder implant applications with good bio compatibility and joint implant performance. The chemical composition of F75 was amenable to AM processing with good printability and therefore was adopted early as a common design grade. In addition to medical, CoCr has found applications in the energy industry for valve components as well as in the aerospace industry for jet engine components. The fuel nozzle component made from CoCr F75 is the quintessential example of this.

Though CoCr F75 is prevalent for medical castings, many specifications for thermal processing remain proprietary. Relatively early in the AM industry, the wrought grade specifications for related CoCr alloys were referred for processing. AMS 5894, referenced in ASTM 3301, is a wrought CoCr variant with higher cobalt than F75. AMS 2774 also refers to solution treatment processing for Stellite 6, that also points to the AMS 5894 specification. ASTM 3301 calls out HIP processing for Co-28 Cr-6 Mo with a note indicating further heat treatment may be necessary. It is common to process HIP followed by separate homogenization treatment.

Project Background

Given the variety of applications, general characterization techniques were observed for mechanical and microstructural consideration. Focus was given to acquiring data typically associated with the benefits of the HIP process such as strength and fatigue. Budgetary limitations of the project precluded formal toughness exploration as well as electron microscopy.

All thermal processing in this study was performed in production HIP as well as vacuum heat treatment units approved for AMS processing at Paulo Cleveland in Willoughby, Ohio. Paulo Cleveland is accredited to NADCAP and AS9100 at this facility for both HIP and heat treatment among other thermal services. Live production equipment provides the best correlation of results relevant to industry service providers of additive manufactured components. High purity argon is the gas medium used in both HIP and vacuum processing.

The broad goal of this study was to explore novel thermal processing of the hot isostatic press and heat treatment process of F75 CoCr, therefore little emphasis was given to testing as-printed or heat treat only conditions. Process design originated from traditional HIP and heat treatment and explored possible alternative and novel designs through HPHT in search of optimized material performance. Additionally, these alternative methods considered improving overall production throughput to further the current industry standards. The designers and providers of AM F75 CoCr may use this as a starting point to consider alternative HIP processes in their applications.

Design of Experiment

Process Design

Baseline processing for CoCr F75 stems from an industry standard HIP cycle for consolidation followed by a homogenization heat treatment. The alloy allows for HIP consolidation at comparable temperatures to heat treatment, except generally with a very slow cooling rate. Traditional industry HIP processing poses limitations on quench rate capability at the end of the cycle due to equipment design. Modern production HIP equipment such as the Quintus QIH-122 used in this study provide fast cooling that has been referred to as "high pressure heat treatment" (HPHT). Leveraging this fast cooling, also called "uniform rapid cooling (URC)," cycle design branched from traditionally divided thermal processing towards novel design to include an effective quench for materials such as CoCr [1,2].

To emulate the "Standard" condition, a HIP cycle of 1,200°C for 4 hours at 100MPa was performed with a slow cooling rate followed by a separate homogenization treatment in a vacuum furnace. Homogenization was performed at 1,190°C for 4 hours followed by a positive pressure argon quench at 220°C per minute.

The next condition combined the two separate processes into one. This "Combined" condition constituted a HPHT cycle of 1,200°C for 4 hours at 100MPa immediately into 4 more hours at 100MPa and 1,190°C followed by a quench in the HIP at 200°C per minute. This eliminated an additional thermal cycle as well as the need to transfer components over to a vacuum furnace.

The "Common" condition cycle consisted of 1,163°C for 4 hours at 100MPa followed by a quench of 200°C per minute. Common condition cycle was performed to reduce time at heat and effectively eliminate the addition of homogenization. This common cycle also aligns with more traditional comingling or "coach" processing, except with a quench—not a feature all service processer can or do provide.

Condition "Improved Performance" further reduced process time, but at higher temperature and pressure. The process was 1,200°C for 2 hours at 200MPa followed by a quench of 300°C per minute. The intention of the improved cycle was to minimize grain growth through a shorter cycle in order to keep strength higher.

The side-by-side representation of the cycle parameters performed can be found in Table 1 where only the standard condition utilizes a vacuum furnace to accomplish homogenization as a separate step from HIP.

Streamlining Process

On improving overall process time for HIP and homogenization for F75 CoCr, there are 3 main factors to consider: separate homogenization cycle elimination, decreasing process door-to-door time, and minimizing logistics between HIP and homogenization.

The elimination of a separate homogenization cycle altogether carries significant value to those providing additively manufactured F75 components. This not only adds value to a HPHT approach, but can speed up time spent in HIP and heat treatment service partners. When parts and material allow, decreasing door-to-door time of the process is a clear path to reducing cost to all in the process stream. The additional logistics of unloading and reloading parts coupled with transporting to other facilities for thermal processing is another clear cost in the process stream. Fortunately, Paulo Cleveland has HIP and vacuum heat treatment under the same roof, however this is not the case with all providers of HIP and may add considerably to cost or overall manufacturing process time.

The different conditions in this study balance possible HPHT alternatives for F75 CoCr while considering the elimination and reduction of homogenization time and minimizing handling and transport logistics. Figure 1 provides a graphical representation of the different condition parameters on the basis of time. The curves represent realistic comparison to scale, but actual processing times may vary from the chart. The standard condition is the base duration and each other HPHT curve reduces total comparable door-to-door time by 29%, 58%, and 72% respectively for combined, common, and improved.

Table 1. Process Condition Parameters

Operation	Process Condition Type			
	Standard	Combined	Common	Improved Performance
HIP	1200C/100MPa/4hr	1200C/100MPa/4hr	1163C/100MPa/4hr	1200C/200MPa/2hr
Homogenization	1190C/4hr	1190C/100MPa/4hr		
Quench	220C/min to 540C	200C/min to 540C	200C/min to 540C	300C/min to 540C

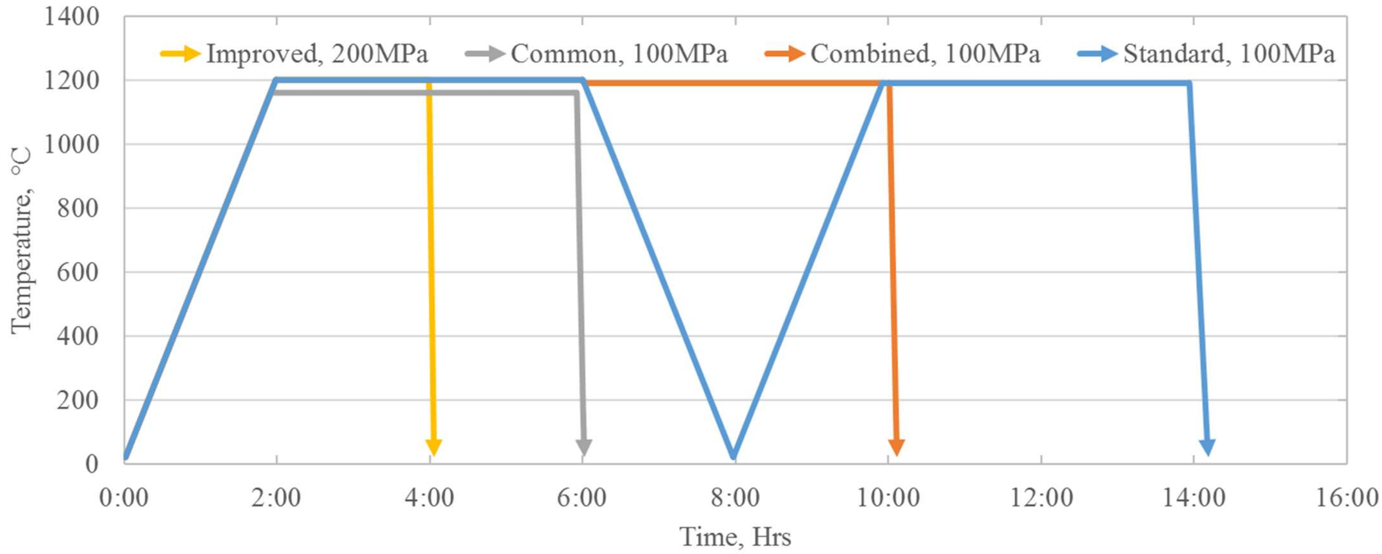

Figure 1: Graphical representation of process condition type. Process time benefit increases moving from right to left.

Samples
The F75 build was done by Stratasys Direct Manufacturing on an EOS M280 under argon gas. The build contained two generic exemplar parts representing flow straighteners from the energy market as well as the following samples:

- 8" vertical x 0.5" diameter cylindrical bars
- 2.5" vertical x 0.5" square Charpy bars

The samples were arranged in groups of 4 around the build plate and were numbered and randomized accordingly to anonymize position across the trial conditions to minimize location bias. Testing direction was along the build direction (z-axis) for tensile and perpendicular to the build direction for fatigue and Charpy testing in order to test the weakest state of the samples. Hardness testing was performed parallel to the build direction. Round bars provided both tensile and fatigue coupons and square bars were used primarily for Charpy testing.

Results and Discussion

Nondestructive Testing (NDT)
Radiographic inspection was performed on the sample materials according to MIL-STD-453C to a sensitivity of 2-2T utilizing film. Tensile specimens were inspected between the grip regions and Charpy specimens were inspected near the notch. All of the specimens were found to be within acceptable limits.

Test samples were also subjected to penetrant inspection in accordance with ASTM E1417 using Type 1, Method A, Level 3 sensitivity penetrant. All of the specimens were found to be acceptable.

Hardness
Hardness testing was performed according to RH-g rev 22 and reported in HRC as reported in Figure 2. All of the conditions met the requirements for typical wrought ASTM F75 of 25-35HRC. Scatter of the results was minimal for all tested conditions with a total spread of 27-31, though there was slightly greater spread for the combined and common cycle conditions. Overall, hardness values are comparable between trial conditions. The common condition exhibited slightly elevated hardness compared to the other conditions, though it is a quite small advantage.

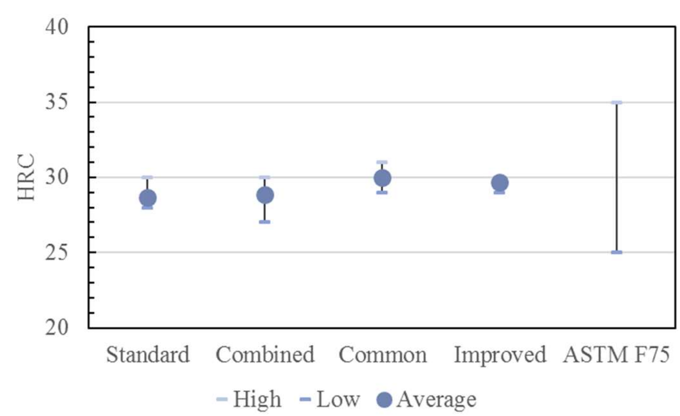

Figure 2: Hardness in HRC by trial condition with ASTM F75 acceptable range for comparison.

Tensile
Round coupons were sectioned and prepared into round tensile bars with a gage diameter of 0.25" per ASTM E8. Testing was performed in accordance with ASTM E8 on five specimens per condition type and stress data was reported in ksi. A full stress-strain curve was generated without removing the extensometer during testing.

Yield stress as 0.2% offset was very similar across all conditions. Data scatter was very low with a total average of 80ksi and sample standard deviation of 2.2. All conditions exceeded the ASTM F75 minimum stress of 65ksi. Each of the novel high pressure heat treatments met or exceeded reported ARCAM typical (electron beam) value of 80ksi [4]. The common condition results showed a slight advantage over the others tested with a maximum individual measurement of 84ksi. Average yield stress for each condition against reference values can be found in Figure 3.

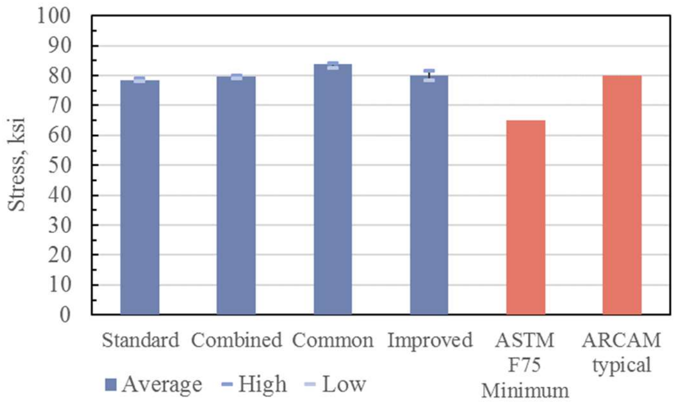

Figure 3: Yield stress in ksi for each tested condition against ASTM and ARCAM typical values [4]. Error bars indicate low and high.

Ultimate tensile strength showed greater variation among results between the different conditions than in yield, but was still overall low in spread. This is likely due to the high strain hardening of CoCr alloys causing localized necking during plastic strain. All conditions well exceeded the ASTM F75 minimum of 95ksi and all conditions exceeded the ARCAM typically reported stress of 140ksi.

The standard condition performed with the highest tensile and elongation of 158ksi and 37% elongation. This offsets the slight disadvantage in yield stress as previously noted. The common condition performed well with the next highest tensile of 150ksi and a moderate level of elongation, 27%. The common and improved conditions performed very close around a measured tensile stress of 146ksi and elongation around 25%. Figure 4 charts the ultimate tensile stress and elongation as described.

Fatigue

High cycle fatigue testing was performed in accordance with ASTM E466. The other portion of the round sample bars not used for tensile testing were sectioned and machined into fatigue coupons with gage diameter of 0.20”. Stress-life fatigue testing was performed at room temperature at a frequency of 30Hz and an R-ratio of 0.1. One specimen was accidentally tested at an R-ratio of -1 and therefore was omitted from the results. The reason to use an R-ratio of 0.1 was to provide a baseline that could be used in the future for specimens cut out of actual parts. Very small specimens are more likely to buckle when loaded under compression, which is the reason for a tension-tension cycle. The 5 samples for each condition were utilized to generate a curve that covers 10,000 to 1,000,000 cycles with the initial S_{max} targeting the middle of the curve. Once that was complete, the samples continued to be cycled to failure or 1,000,000 cycles and then most were repeated until ultimate failure. This method of generating a curve for each condition was intended to provide a side-by-side comparison between the conditions.

No fatigue curves were available for F75 CoCr at the time this project was conducted, the S_{max} of 55ksi was used as 70% of the mean yield stress at 80ksi. Following the accidental run with R-ratio of -1, it was decided to increase the S_{max} to 90ksi.

Figure 5 graphs the applied stress against cycle count in generating the fatigue curves. Overall, the different conditions are similar in performance and given the improved condition crosses from fewer cycles at higher stress to more cycles at lower stress. The common condition appears to be slightly higher than the other conditions, however likely still part of the same overall population. It is interesting to note that CoCr has

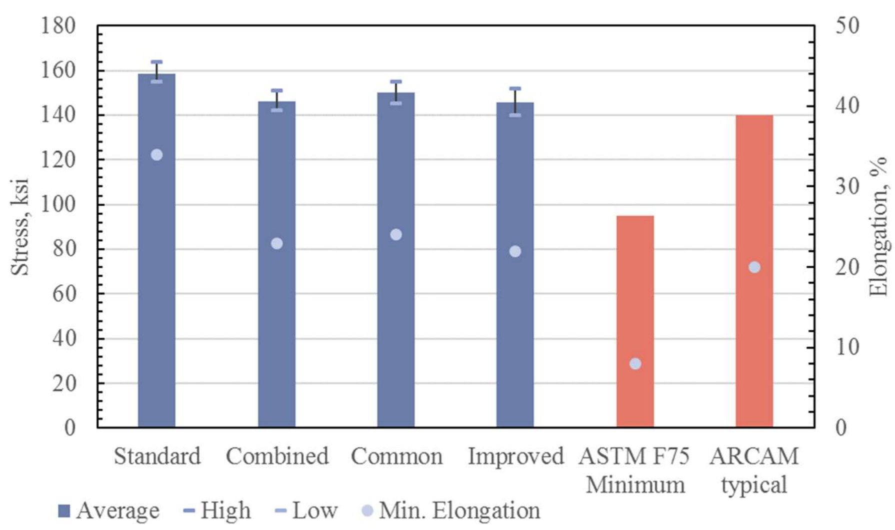

Figure 4: Ultimate tensile stress in ksi for each test condition against ASTM F75 and ARCAM typical values. Error bars indicate low and high. Dot markers indicate elongation in percent.

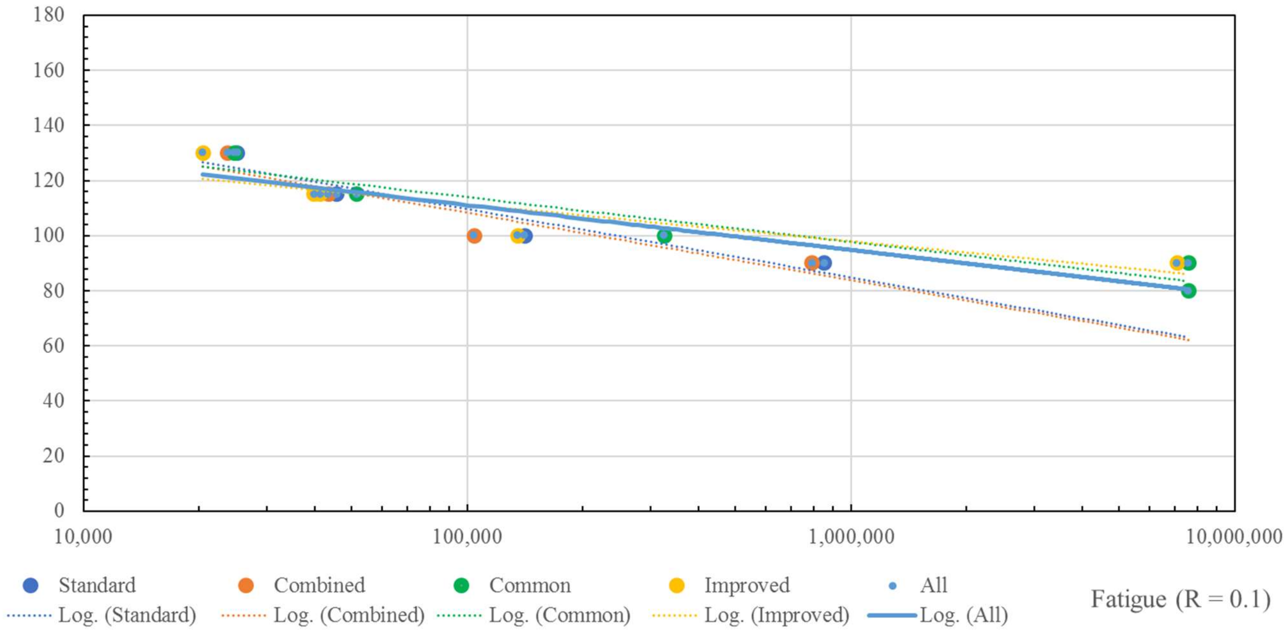

Figure 5: Applied maximum stress in ksi vs number of cycles to failure for each condition.

a relatively high endurance limit and considering the stresses at 100,000 cycles and 1,000,000 cycles against the yield and tensile values for this material, its fatigue performance is impressive. This is likely driven by the strain hardening phenomenon in F75.

Microscopy and Macroscopy

Optical microscopy was performed on the different conditions to observe general differences. Transverse or x-y plane sections were prepared from a portion of the round bar sample. Sections were mounted, polished to 1µm, and etched. An etch of 31% HCl with H_2O_2 periodically dropped on the sample surface was used. The electrochemical rig was setup using graphite electrodes and a power source of 300mA at 6V. Images were captured using PAX-It camera and software on an Olympus GX51 metallograph. Microstructure results were comparable across all samples regarding grain size and distribution of FCC and HCP phases. At the project start, it was anticipated that these might be more different given the temperature and time at heat potentially affecting grain size and homogenization. It does not appear that this was the case. Etch relief inside the grains was a challenge to achieve on the samples, but the standard condition provided a more complete etch. Aside from this difference, the degree of visible HCP plates and grain size was comparable across the different conditions [2]. This agrees with the consistent mechanical performance across conditions. Figure 5 shows a good representation of the different conditions as observed at 200x original magnification

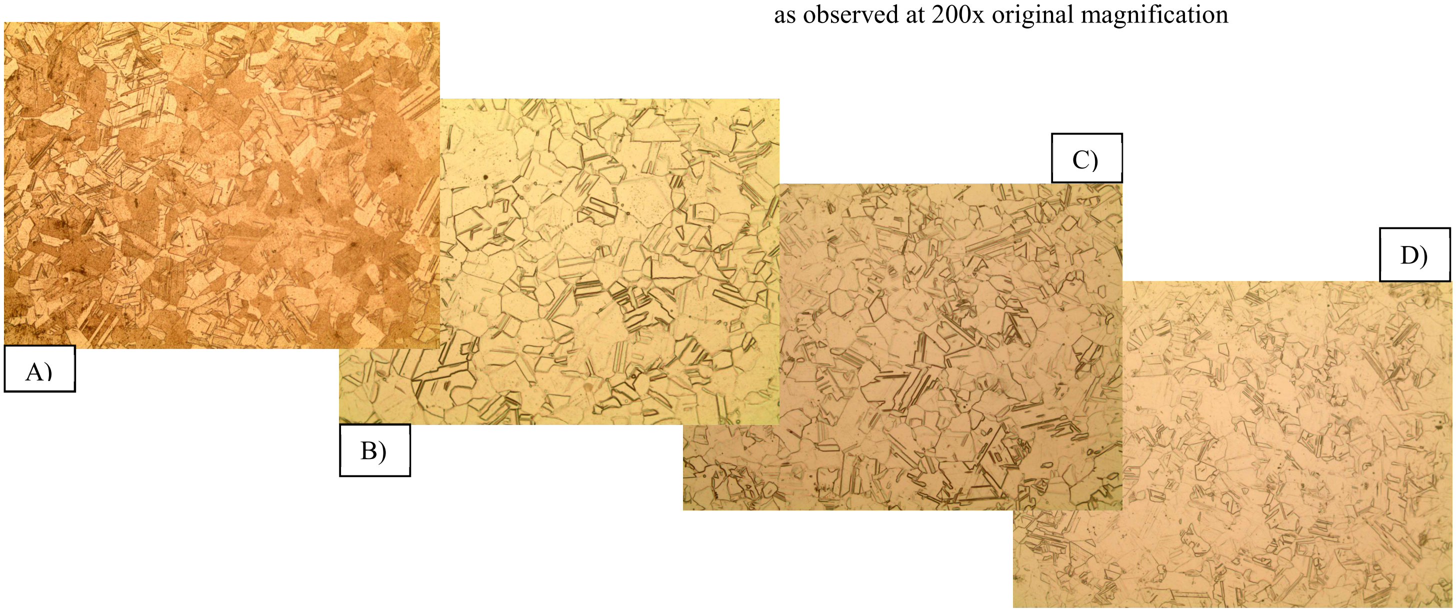

Figure 6: 200x original magnification micrographs for each condition. A) Standard B) Combined C) Common D) Improved Performance

Fatigue fracture surfaces were reviewed on representative specimens with the highest overall performance of strength for each condition. Low magnification macrographs were obtained at approximately 12x using an Olympus SZ61TR with image capture ability. There were no major noticeable differences between the fractures, yet the ductile material provided a more planar surface than typical. The two phase matrix of HCP and FCC is the most likely reason for this planar crack path.

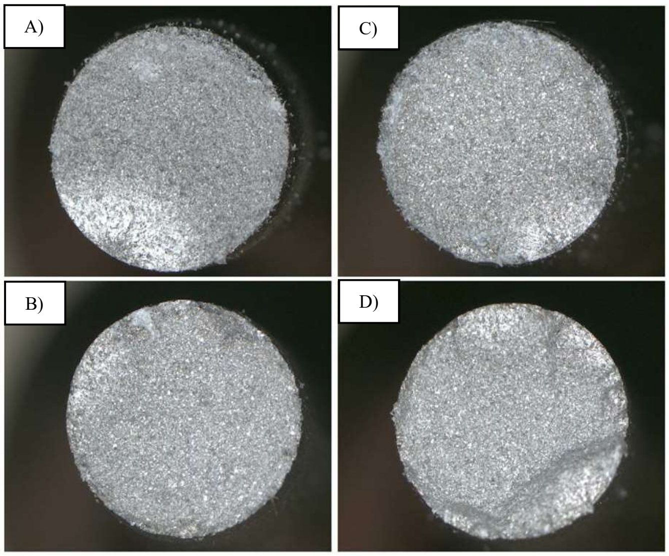

Figure 6: Approximately 12x original magnification macrographs of fatigue fracture surfaces. A) Standard B) Combined C) Common D) Improved Performance

Charpy Impact

Impact testing was performed according to ASTM E23 on 10mm x 10mm rectangular specimens with a V notch. Testing was performed at room temperature. Though charpy testing is an unusual method for testing this composition, it provides a partial metric of toughness that is more economical to dedicated toughness tests. The results of testing may be found in Figure 6, though the main takeaway for this study is the qualitative observation that each performed comparably with no major outliers. One unexplainable observation is that the standard condition exhibited greater elongation and ultimate tensile strength, yet there was not a measured benefit in impact results. ASTM E1820 testing is advisable for further investigation in toughness. An aside comment is that these values are quite good for Charpy results, indicating the F75 CoCr has relatively a high amount of toughness.

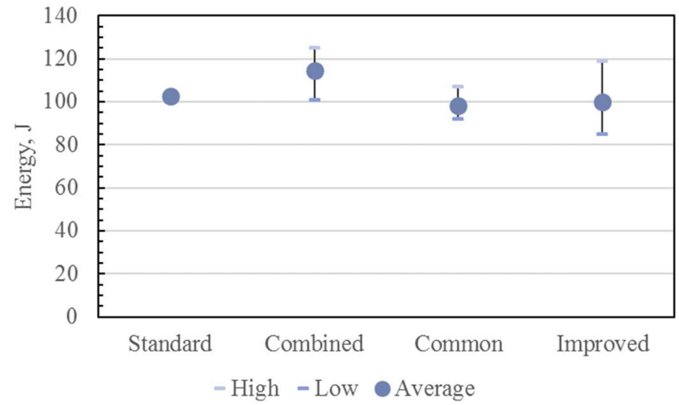

Figure 7. Charpy impact energy for each condition. Error bars are low and high.

Conclusions

Overall, the common condition of quenching at the end of the HIP cycle showed a slight advantage in hardness, yield strength, and fatigue performance. Although additional testing should be conducted to verify in a given application, the common condition recipe should be considered as a viable alternative to the traditional processing route and may provide other benefits to streamlining the production of F75 CoCr AM parts. The originally anticipated "improved performance" condition was found to not provide a clear performance advantage over the standard condition or the common condition as observed.

Considering the three high pressure heat treatment variant conditions against the traditional standard, data comparisons of mechanical properties observed in this study showed that there was no significant degradation. This means that these and potentially other more economically viable methods may be considered for improved turn-around through the elimination of separate homogenization treatment. This stability in performance shows there is flexibility to the designer or AM service provider of F75 CoCr.

Current EBM recommendations in the industry have begun to adapt to a HIP only thermal process and laser based processes could follow [4]. Since this project originated, an alternative powder bed laser fusion cover gas of nitrogen has been documented in application for this alloy. Entrained nitrogen gas has the potential to benefit more than entrained argon through HIP and would be a promising tie to further HPHT investigation [5].

Further work might look into testing not covered in this study including: corrosion resistance, SEM analysis with full fractography, and proper toughness testing. Dimensional implications of eliminating thermal cycling and more uniform quenching in a high pressure heat treatment process are additional worthwhile areas to consider.

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