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Tensile properties of R512E coated Nb—C103 manufactured using laser powder bed fusion (L-PBF)

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ABSTRACT

C103 is a niobium based refractory alloy commonly used in the aerospace industry. To protect the metal from high-temperature oxidizing environments, C103 is often coated with an environmental barrier coating. A common coating for this material is known as R512E, a disilicide slurry applied and cured with heat. This paper aims to determine the effects on mechanical properties of common post processing techniques used on C103 produced via laser powder bed fusion. Tensile specimens were produced in both horizontal and vertical orientations, post processed via hot isostatic pressing, coated, and further heat treatment to simulate a typical operating environment for the coated material. Tensile tests were then conducted at room temperature and compared to ASTM B654 standards for wrought C103. Strength decreased after HIP and coating but remained unchanged after further heat treat. Grain growth was evident after HIP and coat applications which is in direct correlation with decreasing strength and increasing ductility.

1. Introduction

During the Cold War and Space Race of the 1960's, a high temperature material was needed that could handle the operating temperatures of thruster nozzles. The material needed to be able to withstand the thermal shock from resting in the cryogenic atmosphere of space to an operating temperature of 1300 °C just seconds after ignition. Refractory metals have the highest melting points of all the metals but are notoriously heavy. An alloy with a high melting point and low mass was desired. Several companies including Boeing, DuPont, and GE were simultaneously developing alloys for this application using niobium as a base metal, the lightest of the refractory metals. As many as 256 alloys in the C-series (niobium was previously called columbium, Cb) [1] were tested but the alloy which yielded the best combination of formability and high temperature properties was C103, Nb-10Hf-1Ti. Other niobium alloys that emerged successful from that time include FS-85 (Nb-10 W-28Ta-1Zr) and Cb752 (Nb-10 W-2.5Zr).

C103 demonstrates high melting temperatures, good strength at elevated temperatures and low density, all suitable attributes for space propulsion materials [2]. Demonstrating good weldability, this material is suitable for additive manufacturing (AM), specifically, laser powder bed fusion (L-PBF). Thruster nozzles typically have large diameters with thin walls which generate significant waste if machined from wrought bar. These components can also benefit from internal cooling channels that are not feasible to produce using traditional manufacturing methods. Additively manufacturing thrusters to near net shape and machining to finish is a cost-effective way to manufacture these parts, especially with the volatility of hafnium's price and availability. However, refractory metals are extremely susceptible to oxidation and C103 is no exception. Rocket propellants often contain oxidizers which, when combined with the high temperatures of combustion, attack the basemetal forming loose oxide scales and undergo severe dimensional degradation [3]. To protect the material from oxidation under high temperature environments a silicide coating may be considered. Environmental barrier coatings (EBC) are designed to prevent catastrophic degradation of the substrate material under high temperature in air oxidizing environments. A common coating for this application is R512E (Si-20Fe-20Cr) [4,5]. This coating, in slurry form, allows for easy application on large and complex parts [5]. Existing literature presents the effects of cyclic oxidation on annealed sheets of coated C103 on mechanical properties. This study aims to identify the effects of R512E and other common post processing techniques on the mechanical properties of AM C103.

The mechanical properties of AM C103 with R512E coating will be

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evaluated and compared against common post-processing techniques, including hot isostatic pressing (HIP) and two different heat treat procedures. The motivation for this investigation is to demonstrate the effects of heat treatment on coated C103 AM parts.

2. Experimental materials and methods

2.1. Powder characterization

Spherical C103 powder was provided by H.C. Starck Solutions (now Elmet Technologies) that was manufactured using an electrode induction gas atomization (EIGA) process. Powder size distribution (PSD) was analyzed using a Microtrac S3500, providing results for D_{10}, D_{50} and D_{90} as 11, 28 and 47 μm, respectively. Elemental composition of the powder was analyzed using the inductively coupled plasma (ICP) technique and interstitial gas analysis (IGA) was performed to measure oxygen content. The composition of both the powder and AM C103 falls within range of the ASTM standard for B654/B654 M [6]. AM powders commonly have increased levels of oxygen because the powders are passivated for safety which forms oxide layers [6]. Bulk density and Hall flow were measured at 4.9 g/cc and 11 s/50 g, respectively. Theoretical density of C103 is 8.85 g/cc. Scanning electron microscopy (SEM) was performed on a Thermo Fisher Scientific Axia ChemiSEM. SEM images of the feedstock can be seen in Fig. 1.

2.2. Printing

Subscale tensile blanks were manufactured using a Renishaw AM400 in both horizontal and vertical print orientations on a pure titanium substrate. The oxygen setpoint of the machine was 100 ppm with argon as a shielding gas and without substrate heating. Layer height was 30 μm, energy density was 121 J/mm^3 and the scan strategy was rotated 67° every layer. Horizontally printed blanks were removed from the plate with wire electrical discharge machining (EDM) and vertically oriented blanks were printed on supports and tapped off the build plate with a rubber mallet. Tensile blanks, as seen in Fig. 2, were then divided into five groups of three for further post processing. Density of parts were calculated using ASTM B962–17, Archimedes immersion density using 200 proof alcohol at 19°C. As-printed relative density was calculated to be greater than 99.5 %. Chemistry of the starting powder and printed material can be compared to ASTM B654 in Table 1.

2.3. Post processing

All of the tensile blanks were machined to ASTM E8 subscale specifications. Group one serves as an as-printed control with no post processing besides machining. Group two demonstrates the effects of only HIP and was performed on the blanks before machining to eliminate the risk of sagging during HIP. Parameters for HIP were 1593 °C at 103 MPa for 2 h per ASTM F3635–23.

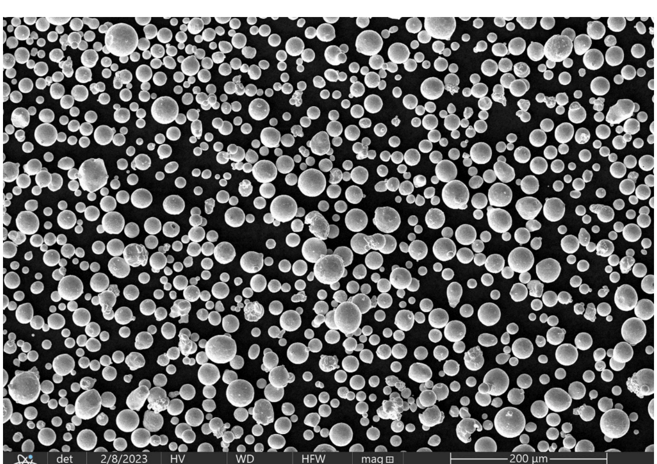

Fig. 1. SEM image of Elmet Technologies C103 powder for L-PBF.

Fig. 2. Vertical and horizontal tensile blanks.

Table 1
Element composition of ASTM sheet, starting powder and printed powder.

Element	ASTM B654 (%wt)	Starting Powder (%wt)	As-printed (%wt)
Nb	Bal.	Bal.	Bal.
Hf	9–11	9.6	9.59
Ti	0.7–1.3	1.0	0.89
Ta	0.5 max	0.2	0.28
W	0.5 max	0.2	0.27
Zr	0.5 max	<0.1	0.07
O	0.035 max	0.027	0.029

Group three took specimens that were HIP'd and had the EBC applied. The vendor of the coating does not disclose the temperature used to apply the coating, but a study by Glass from 1997 suggests that the slurry coating is applied at 1426 °C for 1 h and is assumed for this experiment [7].

Further post processing included vacuum heat treating of group four and five at 1093 °C and 1426 °C for 3.33 h. Heat treat cycles for group four and five will be referred to as HT1 and HT2, respectively, in following figures. Fig. 3 outlines the post processing step for each group. The selected temperatures and pressures replicate the typical operating environment experienced by this material if used for spaceflight applications and 3.33 h is the demonstrated steady state firing duration of a production rocket engine with C103 components, specifically, the Aerojet Rocketdyne R-4D-11. Following heat treatment, all tensile bars were tensile tested at room temperature following ASTM E8 standards.

3. Results and discussion

In this study, the tensile properties of AM C103 that was post processed using common techniques was compared to wrought C103.

The results in Figs. 4 and 5 represent the average of three tensile specimens printed in each orientation compared to the ASTM B654 standard for wrought C103. As-printed C103 met or exceeded the specifications for ultimate tensile strength (UTS), yield strength (YS) and elongation (ε) for both vertical and horizontal print orientations. Specimens that were HIP'd resulted in lower tensile properties and the application of the coating further lowered the strength of the material while raising the ductility. Further heat treatment of the HIP + Coated specimens appeared to have little effect on the mechanical properties of the material.

Fig. 3. Post Processing for Each Group of Printed Tensile Blanks.

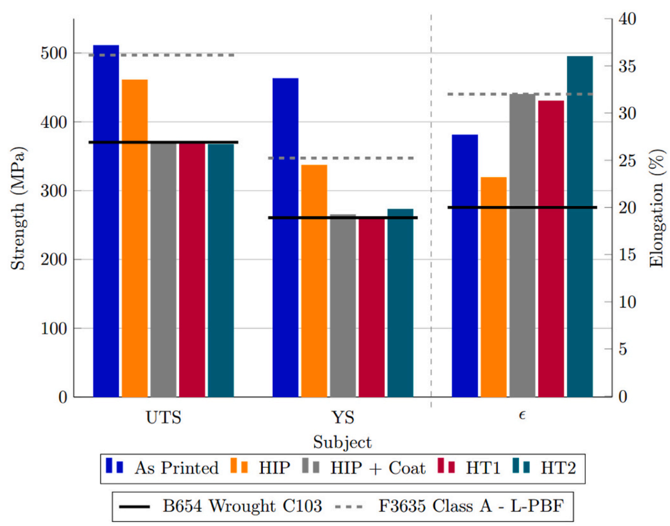

Fig. 4. Tensile properties of horizontally printed tensile bars.

3.1. *Microstructure*

A cross-section of a sacrificial sample from the same build plate was analyzed. EBC thickness measured 125 μm where half of the coating thickness is fused to the new material and the other half is added to the surface, as indicated by the porous material in Figs. 6. Through-thickness cracking is apparent in the coating caused by differing coefficient of thermal expansion (CTE) between the base metal and coating. This is typical of silicide coatings applied to Nb, Mo and W alloys [3]. The CTE of $NbSi2$ is higher than that of the base metal niobium, 7.3–11.7 μm°C-1 and 7–8 μm°C-1, respectively [3].

Assuming an application temperature of 1200-1400 °C, the coating experiences tensile stresses during the cooling process from application heat treat to room temperature. NbSi2 is inherently brittle and caused these through-thickness cracks [3]. Kumawat et al. conducted energy-dispersive X-ray spectroscopy (EDS) analysis near the cracks to determine if oxygen was able to penetrate the base material after vacuum heat treatment. The presence of oxygen was not detected suggesting that the interaction of oxygen and niobium did not occur during the coating formation heat treatment. This was assumed to be true for the current study.

Tensile bar grip ends that had been HIP and coated were analyzed using electron backscatter diffraction (EBSD) to analyze the crystallographic texture and grain structure as shown in Figs. 7. Although only the gauge length of the tensile bars had coating applied, the entire tensile bar was subject to the temperatures required to cure the slurry. Planes normal to build direction (BD) and perpendicular to BD were observed. EBSD inverse pole figure (IPF) taken normal to BD reveals random yet equiaxed grains. Perpendicular to BD reveals columnar grains favoring ⟨112⟩ crystal orientation. The average grain size normal to and perpendicular to BD was 159 μm and 164 μm, respectively. High temperatures from HIP and coating processes have been shown to cause grain grown in L-PBF AM parts and were evidenced in this experiment [8].

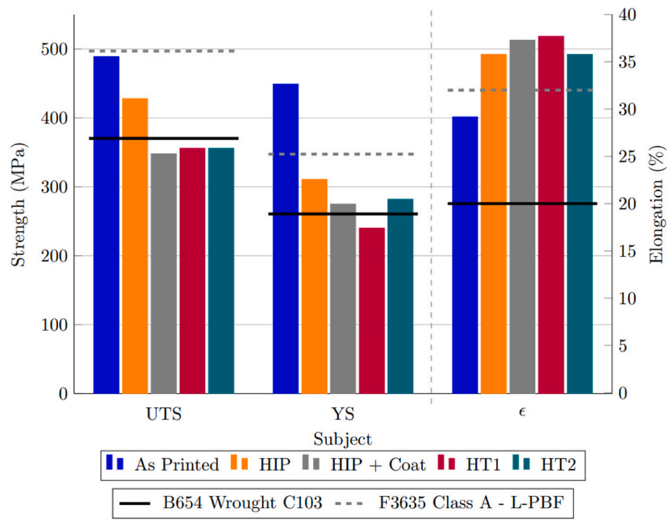

Fig. 5. Tensile properties of vertically printed tensile bars.

3.2. Grain growth

Grain size is a key factor that determines the properties of metal alloys and can affect tensile strength, ductility, fatigue, hardness, thermal conductivity, etc. [9]. To determine if grain size was a cause for the change in tensile properties, grip ends from each of the tensile bars were etched and polished to measure grain size across the five groups. Table 2 shows the average grain diameters of each post processing step. C103 in the as-printed condition had the finest grain structure. Grain size grew roughly 250 % after hot isostatic pressing while yield strength decreased by 31 %. Grains grew another 15 % after the application of the coating and again the yield strength decreased, by 12 %. Grain size was not severely affected by HT1, although HT2 increased the grain size a further 15 % but had insignificant effect on tensile properties. The Hall-Petch relationship can be used to describe the relationship between yield strength and grain diameter using eq. 1, where d is the average grain diameter, k is a material dependent constant and σ_o is the friction stress.

$$\sigma_y = \sigma_o + k \Big/ \sqrt{(d)} \tag{1}$$

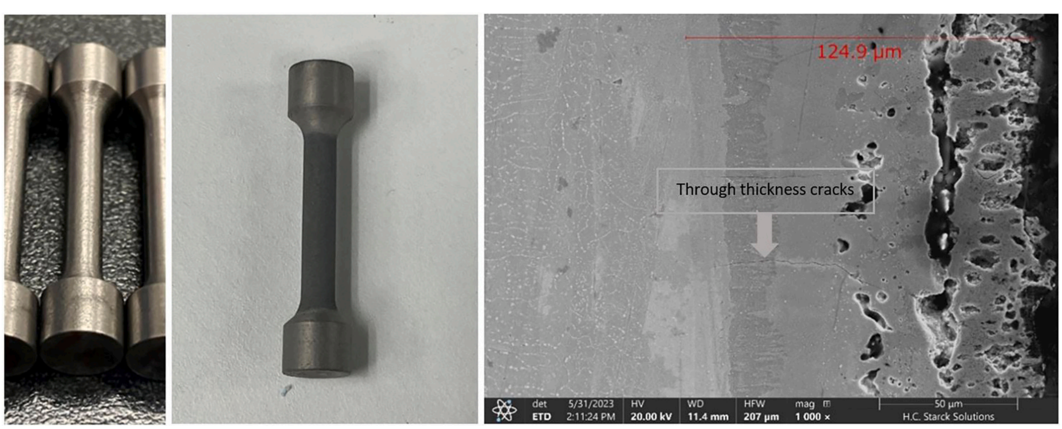

Fig. 6. Machined tensile bars. Middle: Machined and coated tensile bars. Right: SEM cross section of coated AM sample.

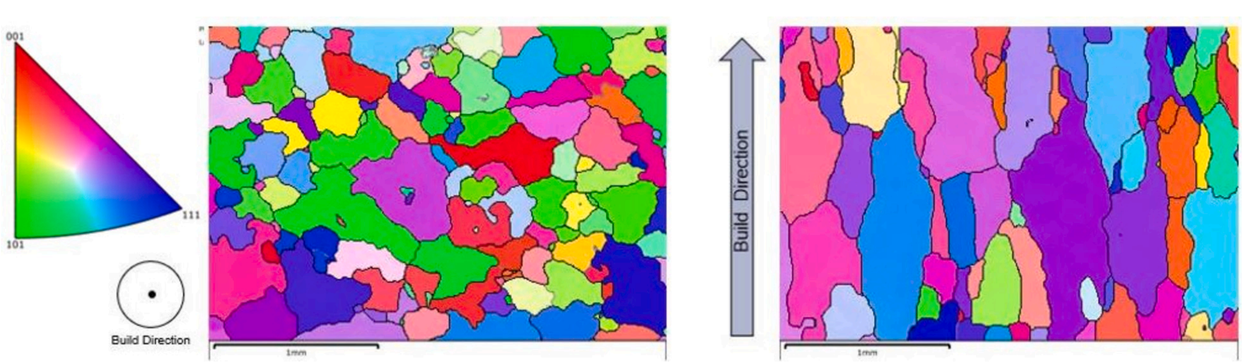

Fig. 7. Inverse pole figures taken normal to build direction (left) and perpendicular to build direction (right).

Table 2
Grain size of vertically printed specimens after post processing steps.

	As-printed	HIP	HIP + Coat	HT1	HT2
Normal to BD (μm)	58	142	159	158	184
Perpendicular to BD (μm)	63	173	164	169	199

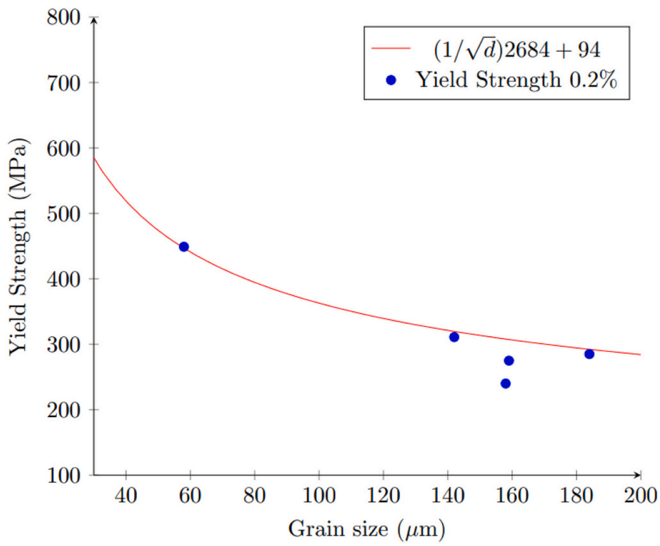

Fig. 8. Hall-Petch curve fit of yield strength vs grain size.

Raw tensile test data was plotted on a true stress vs true strain curve to calculate σ_o and k. These values were then used to plot the Hall-Petch curve fit of the measured yield strength from each of the five groups against expected yield strength across various grain sizes as seen in Fig. 8. This curve fit suggests that as grain size gets larger its effect on yield strength is reduced. As-printed tensile bars from group one had the smallest grain size and the highest strength. Grain size grew with post processing treatments, however, the effect of grain size on strength is less pronounced as grain size increased.

4. Conclusion

The tensile properties of C103 produced via L-PBF were successfully analyzed. If C103 is to be used in spaceflight applications, specifically in an oxidizing environment, the part is likely to be HIP'd and an environmental barrier coating is likely to be applied by the end user. The effects of these treatments have detrimental effects on the strength of this material. This research highlighted the effects of HIP, HIP + Coat, and HIP + Coat + vacuum heat treat and is highlighted below:

1. As printed C103 is capable of meeting ASTM standards of wrought material for strength and elongation.
2. HIP'd material showed significant grain growth and a decrease in strength yet continued to exhibit strength higher than the minimum requirement wrought material.
3. The application of R512E again caused grain growth and lower strength, almost equal to wrought C103. EBC vendors should publish the application temperature and duration as it has a direct effect on the mechanical properties that the part designer may not be aware of.

4.1. Comparing to F3635–23 standards

Per ASTM F3635–23, Class A parts in this method destined for spaceflight applications shall be processed by HIP and require a grain size of 3 to 5 or finer with UTS of 497 MPa, YS at 0.2 % offset of 347 MPa and elongation of 32 %. In the current study, the HIP procedure caused grain growth that exceeded the 3 to 5 (0.065–0.130 mm) requirement. This grain growth resulted in a decrease of strength that caused the material to fail the published standards for UTS and YS.

CRediT authorship contribution statement

Tyler DuMez: Writing – original draft. **Michael T. Stawovy:** Supervision, Writing – review & editing. **Scott Ohm:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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