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¹ Tailoring Thermal Transport Properties by Inducing Surface ² Oxidation Reactions in Bulk Metal Composites

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14 (LFA) at incrementally elevated temperatures. Focused ion beam (FIB) slicing of 15 the substrate coupled with scanning electron microscopy (SEM) and energy 16 dispersive X-ray spectroscopy (EDX) show that the substrate oxidized only along 17 the outer 20 μ m of the bulk surface. The layer thickness is significantly less than

16 dispersive X-ray spectroscopy (EDX) show that the substrate oxidized only along 17 the outer 20 μ m of the bulk surface. The layer thickness is significantly less than 18 typical TBCs that can range from 50 to 300 μ m yet the 20 μ m coating still achieves a dramatic reduction in thermal transport 19 properties. Additionally, thermal analysis reveals a sequence of exothermic reactions starting at 439 °C that include both 20 intermetallic (i.e., ZrAl₃) and oxidation (i.e., Al₂O₃ and ZrO) reactions suggesting continuous surface bonding at the coating-metal 21 interface. The onset of exothermic activity coincides with the transition in thermal properties measured using LFA. These results 22 show that surface oxidation reactions could be used to dramatically alter the thermal transport properties of a metal substrate.

23 KEYWORDS: thermal conductivity, thermal barrier coating, interface chemistry, zirconia, laser flash analysis

1. INTRODUCTION

24 Thermal barrier coatings (TBCs) are typically composed of 25 partially yttria-stabilized zirconia (YSZ) that may be doped 26 with aluminates or zirconates to establish a large temperature 27 drop (several 100 K) across the ceramic layer.¹ The coating 28 purposefully protects the metal substrate from high operating 29 temperatures and can extend the lifetime of a component such 30 as in gas turbine applications.² The ability to alter the bulk 31 thermal properties of a metal by applying a surface coating has 32 applications beyond static components such as combustor cans 33 and vane platforms. For example, metals can be used as energy-34 generating fuels in applications such as structural reactive 35 materials (SRM).^{4,5} An SRM is a metallic substrate that may be 36 used in place of an inert steel component in defense 37 applications such as ordnance technologies. For SRM 38 applications, applying a TBC could enable thermal control of 39 the SRM in reactive or high temperature environments. The 40 science of TBCs may be applied in unique ways to tailor a 41 metal's response to suit a specific environment without 42 sacrificing the bulk characteristics of the metal. The science 43 of surface reactions induced deliberately to alter bulk thermal 44 properties has fundamental scientific merit and can influence 45 material development for a wide range of applications.

This study introduces a twist to the common TBC by 46 creating the coating in situ by inducing surface reactions at 47 moderately elevated temperatures. More traditionally, TBCs 48 are deposited on a metal substrate using electron beam 49 physical vapor deposition or atmospheric plasma spraying.^{6,7} 50 The TBC can be $50-300 \mu$ m thick and is also a duplex-type 51 system with a metallic bond coat underlying a ceramic topcoat. 52 The bond coat improves bonding between the ceramic topcoat 53 and metal substrate, but the topcoat acts as the thermal barrier 54 and usually includes alumina or zirconia to reduce thermal 55 transport.^{7,8} In this study, the metallic substrate was composed 56 of aluminum and zirconium (Al–Zr) powder compacts that 57 were hot isostatically pressed (HIP) into consolidated metal 58 substrates. The metal composite was selected to exploit the 59 insulating properties of alumina and zirconia that form at the 60

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61 surface upon oxidation reactions and are commonly used 62 ceramics in TBC applications.^{1,8}

The goal of this study was to assess the extent of reduction 63 64 in thermal transport properties that may be achieved by 65 inducing surface oxidation reactions on a metal substrate. The 66 objective was to subject a metal substrate to elevated 67 temperatures and incrementally measure variations in thermal 68 transport properties of the bulk material. A second objective 69 was to use microscopy to resolve the microstructure of the 70 surface and quantify the thickness of the altered surface 71 chemistry in relation to the bulk metal. A final objective was to 72 measure thermal reactive behavior for the metal substrate to 73 validate product species formation that may populate the 74 surface coating. To accomplish these objectives, laser flash 75 analysis (LFA) was used to quantify thermal properties as a 76 function of elevated temperature followed by detailed 77 microscopy coupled with thermal analysis of reaction behavior 78 using differential scanning calorimetry (DSC). This study 79 provides an alternative strategy for applying a TBC by tailoring 80 surface chemistry to alter the bulk properties of the metal and 81 extends the traditional thinking about the applications for a 82 TBC.

2. EXPERIMENTAL SECTION

2.1. Materials. Precursor materials were all obtained from Sigma-84 Aldrich (St. Louis, MO) and include 10 μ m average diameter Al 85 powder and 5 μ m average diameter Zr powder. The powders were 86 mixed at a 3:2 molar ratio (or 30:70 mass ratio) of Al:Zr for 87 consistency. The mixture was pressed via hot isostatic pressing (HIP) 88 at a low temperature (i.e., <300 °C). The entire HIP processing 99 duration does not exceed 2 h and the material is exposed to a peak 90 temperature for less than 30 min. Powder processing consolidates the 91 material into a substrate with 98% theoretical maximum density 92 (TMD). The compacts were cylindrical pellets 12.6 mm in diameter 93 and 2 mm thick, as illustrated in Figure 1a.



Figure 1. (a) Photograph of the pelletized substrate. (b) SEM image of substrate after HIP consolidation with EDX mapping showing Zr (red) and Al (brown) locations and (c) the corresponding backscattered SEM image.

The pellet substrates were analyzed to assess intermetallic formation that may have occurred during the compaction process using a Thermo Scientific Phenom ProX Desktop scanning electron microscope (SEM). The SEM was equipped with a backscatter electron detector (BSD) and inherent energy-dispersive X-ray (EDX) system operated at 15 kV and set to map current intensity. The images shown in Figure 1b, c include an EDX species map (Figure 101 1b) that illustrates a well-mixed powder consolidated Al:Zr substrate with distinctly separated Zr (red) regions within the Al matrix (brown) alongside the corresponding SEM image showing microid structure (Figure 1c). Notice the softer Al metal binds the matrix together, whereas the harder Zr particles remain discretely separated. Figure 1 demonstrates no apparent intermetallic species at particle poundaries resulting from consolidation. The consolidated pellet was used for Laser Flash Analysis (LFA) 108 measurements of thermal properties, but Differential Scanning 109 Calorimetry (DSC) measurements required powder samples. There-110 fore, some of the substrates were also fragmented using a vertical mill. 111 The fragments have a flakelike morphology with an average 500– 112 1000 μ m size, shown in Figure 2. It is noted that the powders used in 113 f2 the DSC are an order of magnitude larger than the precursor powders 114 of pure metals. Notice in Figure 2a the flakelike microstructure of the 115 shavings can be as long as 1000 μ m while Figure 2b shows a higher-116 resolution image of the microstructure within a single shaving 117 (corrugated top surface) and Figure 2c illustrates the discretely 118 separated Al and Zr species. In Figure 2d–f, the SEM images are of 119 the distal end of Al:Zr fragments. The shavings appear to be 120 approximately 30–50 μ m thick based on these images and maintain a 121 3:2 Al:Zr molar ratio throughout the cross-section. 122

Further confirmation that HIP consolidation of powders avoided 123 formation of intermetallic species is shown by XRD patterns in Figure 124 f3 3. The composition is consistent with the precursor materials and 125 f3 includes about 57 wt % Zr, 37 wt % Al, and 5 wt % zirconium hydride 126 (ZrH). On the basis of the SEM-EDS analysis and XRD analysis of 127 the precursor material shown in Figures 1–3, intermetallic species 128 formed during the HIP consolidation process are not measurable, 129 indicating negligibly small concentrations. 130

2.2. Light Flash Analyzer (LFA). Thermal diffusivity was 131 measured at 25, 100, 200, 300, 400, 500, and 600 °C by the flash 132 method using a NETZSCH LFA 467 HT HyperFlash instrument. 133 The substrate was aligned in a holder between a Xenon Flash Tube 134 and an indium antimonide (InSb) IR detector in a furnace with an 135 operating temperature ranging from 20 to 1250 °C. Once the 136 substrate was stabilized at the desired temperature (i.e., a 5 min hold 137 time), the flash lamp was fired five times over a span of a few minutes 138 and the transient thermal data recorded. The flash energy was 139 absorbed by the front surface of the substrate, causing a heat pulse to 140 travel through the 2 mm thick substrate. The resulting back surface 141 temperature rise was small (i.e., 0.5-2 °C) and monitored with an IR 142 detector. The temperature rise signal versus time was amplified and 143 recorded with a high-speed A/D converter (2 MHz). The specific 144 heat values were measured using a graphite reference sample for 145 calibration. Density was not corrected because of thermal expansion 146 and thermal conductivity was calculated from the NETZSCH LFA 147 software. Multiple tests were performed to establish reproducibility of 148 the results and the standard deviation in measurements was less than 149 0.5%. 150

2.3. Focused Ion Beam/Scanning Electron Microscopy/ 151 Energy-Dispersive X-ray (FIB/SEM/EDX) Analysis. FIB/SEM/ 152 EDX analysis was performed on the substrate that was heated to 500 153 °C then cooled to room temperature. The analysis was performed to 154 identify the spatial distribution of oxygen-containing species and 155 extent of surface oxidation reactions. The gallium ion beam generated 156 by a Hitachi NB5000 focused ion and electron beam (dual-beam FIB-157 SEM) system was used to fabricate a vertically oriented 80 μ m wide × 158 40 μ m deep "window" (i.e., cross section) on the top of the pellet 159 (Figure 4a). The 80 μ m wide × 65 μ m high "trench" was fabricated in 160 f4 front of the "window" (Figure 4a) to enable SEM imaging (Figure 4b) 161 and X-ray mapping of the entire depth of this "window". X-ray 162 mapping was accomplished using an energy-dispersive X-ray 163 spectrometer (EDX) attached to the FIB-SEM system. 164

2.4. Differential Scanning Calorimetry (DSC) and Thermog-**1**65 **ravimetric Analysis (TGA).** Thermal analysis was performed with a 166 NETZSCH Jupiter simultaneous thermal analyzer (STA) 449 which 167 combines a differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). Fragmented powder mass was maintained 169 constant at 10 mg and contained in an alumina crucible sealed with a 170 lid that has a pinhole opening. Samples were heated from 50 to 1500 171 °C at 10 °C/min in an atmosphere with 80% oxygen and 20% argon. 172 Experiments were performed in triplicate to ensure repeatability and 173 results were replicated within 2% of the reported data with standard 174 deviations reported. The DSC and TGA data were processed with 175 NETZSCH Universal Analysis software to determine onset temperatures and enthalpy of reaction. 177

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Figure 2. (a) Macroscopic view of fragments, (b) individual shaving plane view, (c) edge view, (d-g) side views showing (d, e) macroscopic and (f, g) microscopic perspectives with (g) color mapping at surface, (h) higher-resolution SEM image of a single shaving (top view) with inset EDX color line scan along the dashed line indicated by an arrow in the image showing variation in Al (blue) and Zr (red) concentration in the vertical direction across the image.



Figure 3. Powder XRD patterns of powder precombustion with primary peaks labeled. Concentrations from Rietveld refinement analysis using whole pattern fitting show concentrations consistent with precursor materials (57 wt % Zr, 38 wt % Al, 6 wt % ZrH).

2.5. X-ray Diffraction (XRD) Analysis. X-ray diffraction (PXRD) analysis was performed on the substrates pre- and postheating to 500 ¹⁷⁹ or C then cooled to room temperature. It is noted that X-rays only ¹⁸¹ penetrate 30–50 μ m into the pellet such that this analysis was ¹⁸² performed purposefully to assess the concentration of species near the ¹⁸³ surface of the heated pellet. An XRD analysis was also performed on ¹⁸⁴ pre- and postheated powders. It is noted that the powder samples were lightly ground with a mortar and pestle in the XRD powder 185 sample carrier to reduce particle size such that diffraction signals were 186 obtained equally from the bulk and surface of the particles. 187

Powder fragments were heated to either 600 or 1000 $^{\circ}$ C in the 188 DSC-TGA at a rate of 10 $^{\circ}$ C/min in an atmosphere with 80% oxygen 189 and 20% argon, then cooled to room temperature according to the 190 cooling curves shown in Figure 5. Cooling was controlled within the 191 f5



Figure 5. Cooling curve for 600 $^{\circ}$ C (green curve) and 1000 $^{\circ}$ C (red curve) heating temperatures.

DSC-TGA instrument by convective air. The purpose of the heating 192 and cooling treatment was to quench reactions at 600 or 1000 $^\circ$ C and 193



Figure 4. (a) FIB secondary electron top-view image of the 80 μ m wide × 40 μ m deep "window" (i.e., cross section) and the 80 μ m wide × 65 μ m high "trench" fabricated on the top of substrate. (b) SEM image of the 80 μ m wide x 40 μ m deep "window" (i.e., cross section) acquired in the secondary electron imaging mode at 5 kV acceleration voltage. The top and bottom portions of the SEM image show the top surface unprocessed by FIB-SEM.



Figure 6. Laser flash analyzer (LFA) measurements of (a) thermal diffusivity and (b) thermal conductivity as a function of temperature. Multiple curves are shown from triplicate sample tests for repeatability and standard deviation in measured values are less than 0.5%.

194 quantify crystalline phases of material formed at the respective 195 temperatures corresponding to exothermic events in the DSC-TGA 196 analyses. This additional XRD analysis provided insight on the reaction pathways favored at low (600 °C) and high (1000 °C) 197 temperatures that are specific to HIP consolidated Al-Zr materials. 198 A Rigaku MiniFlex II powder diffractometer utilizing Cu K α 199 200 radiation (1.5418 Å) was operated in continuous θ -2 θ mode from 5 201 to 90° 2θ with Bragg–Brentano geometry for all XRD analysis. The 202 step size was 0.02° with a collection time ranging from 0.1 to $0.5^{\circ}/$ min depending upon the sample. The Rietveld refinement of peak 203 intensity (height), width, and position were used to identify 204 205 composition of the crystalline species. The MDI Jade V9.1.1 software 206 package and ICDD PDF 4+ database were used in conjunction for the 207 identification of phases and to provided semiquantitative data analysis 208 through the use of Rietveld refinements (least-squares approach to 209 match theoretical and experimental XRD data).

3. RESULTS AND DISCUSSION

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210 Figure 6a shows thermal diffusivity and Figure 6b shows 211 thermal conductivity as a function of temperature. As 212 temperature increases there is a gradual reduction in thermal 213 diffusivity and corresponding increase in thermal conductivity 214 up to 400 °C. Between 400 and 500 °C, thermal properties 215 dramatically reduce (i.e., by 75–80%) and remain low as 216 temperature continues to increase to 600 °C. The dramatic 217 reduction in thermal properties corresponds with oxidation 218 reactions that would produce alumina and zirconia that have 219 highly insulating properties.

To understand the heat transfer process occurring in Figure 220 221 6, further analyses of the composition and microstructure were 222 performed before and after heat treatment. The first series of 223 characterization studies used XRD patterns before and after 224 heat treatment to resolve the species at the outer surface of the 225 substrate. The penetration depth of this X-rays in this analysis 226 is $30-50 \ \mu m$ depending on the angle of incidence, whereas the 227 substrate has a 2 mm thickness such that the species detected 228 are representative of the outer surface. Figure 7 shows the 229 pattern overlay to compare the intensity of peaks and 230 summarizes species concentrations determined from the 231 Rietveld refinement analysis. Figure 7 confirms the presence $_{232}$ of oxide species that include Al_2O_3 (28.8 wt %) and ZrO_2 (8.2 233 wt %) post heating to 500 °C but also indicates a high 234 concentration of Zr and Al. Therefore, to confirm that the 235 metal oxides were localized on the outer surface of the pellet 236 further resolution of the microstructure was performed using a 237 FIB to slice the substrate into a microscale sample that could 238 be analyzed with SEM and EDX.



Figure 7. XRD patterns from pre- (red curve) and post-500 °C heating (blue curve) of the substrate for 5 min duration achieving thermal equilibrium. Heating to 500 °C produced relatively high concentrations of metal oxides, i.e., 28 wt % Al_2O_3 , 8.2 wt % ZrO_2 , 32.7 wt % Zr, 15.8 wt % Al, 7.8 wt % Al_xZr_y , compared to before heating, 48 wt % Zr and 28% wt % Al, according to Rietveld Refinement analysis using whole pattern fitting.

Elemental maps of the entire "window" are shown in Figure 239 f8 as well as the approximately 40 μ m × 20 and 30 μ m × 15 μ m 240 f8 upper left side portions of this "window" are provided in the 241 Supporting Information. To correctly display SEM images and 242 elemental maps of the fabricated cross section in the vertical 243 direction, we used the cross-section tilt compensation function 244 of the FIB-SEM software to account for the inclination of the 245 SEM column. In all cases, species containing oxygen are 246 limited to the top surface of pellet unprocessed by FIB-SEM. 247 Results show the oxide species are locally formed at the outer 248 edges of the pellet whereas intermetallic species form in the 249 pellet interior. The thickness of the oxidized layer is estimated 250 from these elemental maps and is approximately 20 μ m. 251

The processes of oxidation and intermetallic reactions were 252 further analyzed using DSC with TGA. Figure 9 shows heat 253 f9 flow as a function of temperature from the DSC analysis and 254 corresponding mass change measured simultaneously. Experi- 255 ments were performed in triplicate and the standard deviations 256 from reported values are within 1.0 °C for onset temperature, 257 1.0 J/g for enthalpy, and 0.5 wt % for mass gain. 258



Figure 8. SEM imaging/EDX mapping of the entire 80 μ m wide × 40 μ m deep "window" fabricated on the top of the pellet. (a) SEM image acquired in the secondary electron imaging mode at 20 kV acceleration voltage used for X-ray mapping. Elemental colored maps obtained from EDX mapping: (b) oxygen in red, (c) aluminum in purple, and (d) zirconium in blue (EDX detection limit within 0.1 wt %). The top and bottom parts in a–d show the unprocessed top surface of the pellet. Triangular areas on the right side of the maps in (c) and (d) are devoid of information due to X-rays that are emitted from this region being obstructed by the wall of the "trench". The same triangular area can be expected on the right side of the map in (b). Elemental maps show that oxide species are localized near the surface of the pellet.



Figure 9. Heat flow (black curve) and mass change (red curve) as a function of temperature in 80% oxygen and 20% argon environment and at 10 $^{\circ}$ C/min heating rate.

The onset temperature of the first exothermic event is 442 2.59 °C with an exothermic enthalpy of 390 J/g. The mass gain 260 261 onset is 591 °C and at significantly higher temperature (i.e., $_{262} \Delta T > 100$ °C) than the onset of exothermic reaction. The delayed onset temperature for mass gain suggests that 2.63 264 intermetallic reactions initiate the first exothermic event in 265 Figure 9 because recombination reactions within the metal 266 composite would not add mass. Following the first exothermic 267 event, a second exothermic event with smaller enthalpies of 24.3 J/g and onset temperature of 637 °C. The second 268 exothermic event includes oxidation because mass gain 2.69 270 continues throughout this temperature range in Figure 9. 271 The two exothermic events in Figure 9 suggest that surface 272 reactions may be multilayered with an inner layer of 273 intermetallic species and an outer layer of metal oxide species. 274 Similarly, traditional TBCs are also duplex type configurations 275 with an underlaying bonding coat securing a ceramic topcoat.

The results in Figures 8–9 suggest this in situ development of 276 a TBC may also provide the coating with additional structural 277 integrity associated with spray coating and laser deposition 278 processing techniques. Further studies on interfacial bonding 279 are needed to investigate that finding more thoroughly. 280

The XRD patterns for fragmented powders heated to 600 °C 281 (i.e., after the first exothermic event in Figure 9) or 1000 °C 282 (i.e., after the second exothermic event in Figure 9) are 283 provided in Figure 10. When the samples were cooled from 284 f10 600 °C (i.e., after the exothermic event in Figure 9), the 285 products are mainly ZrAl₃, Zr, and Al along with some 286 aluminum and zirconium oxides in smaller concentrations. The 287 data in Figure 10 are consistent with Figure 9, indicating 288 mainly intermetallic reactions in the first exothermic event 289 followed by some oxidation of the metals. The small 290 concentrations of metal oxides in Figure 10 also support the 291 results in Figure 6 that show oxidation reactions are narrowly 292 limited to within 20 μ m of the pellet surface and can occur at 293 temperatures between 400 and 500 °C. At elevated temper- 294 atures associated with the second exothermic event in Figure 9, 295 both oxides are present (Figure 10). Despite the moderately 296 high concentration of oxide species that generate more calorific 297 energy than intermetallic reactions, enthalpy is lower than in 298 the first exothermic event, but the heat flow curve gradually 299 increases with increasing temperature, indicating oxidation 300 growth continues at elevated temperatures. 301

Figure 11 shows data for thermal conductivities of various Al 302 f11 and Zr species indicated in Figures 7 and 10^{9-11} relative to the 303 measured value from Figure 6 (labeled AlZr_{LFA}) and a 304 weighted average for the stoichiometric mixture of pure Al 305 and Zr (labeled AlZr_{avg}). Intermetallic species such as ZrAl₃⁹ 306 would increase the thermal conductivity relative to the 307 measured value. Species with a higher atomic concentration 308 of Zr may decrease thermal conductivity relative to Al rich 309 species and internally may contribute to a lower thermal 310 conductivity, although Figure 10 shows no sign of Zr-rich 311 intermetallic species at 600 °C. In this powder compact, Al is a 312 softer metal than Zr and spreads or binds the matrix together 313 (see Figure 1). The Al may be more exposed to oxygen, 314 thereby facilitating Al₂O₃ formation compared with ZrO₂. As 315 expected, both Al₂O₃ and ZrO₂ exhibit thermal conductivities 316 lower than the measured value, with ZrO₂ on the order of 2 317 W/mK^{10} and Al_2O_3 on the order of 20 $W/mK.^{11}$ An ${}_{318}$ interesting observation in Figure 6 is that the Al₂O₃ thermal 319 conductivity is a stronger function of temperature than ZrO₂ 320 up to 400 $^{\circ}$ C and then Al₂O₃ plateaus at an average of 10 W/ 321 mK. At elevated temperatures (i.e., >400 °C), both metal 322 oxides exhibit similar thermal conductivities (i.e., 2-10 W/ 323 mK) and clearly contribute to the reduction in measured 324 thermal conductivity more than intermetallic species. 325

CONCLUSIONS

The highlight of this study is that we made a TBC without ³²⁷ external application but instead intrinsically through mild ³²⁸ thermal processing of the base material, and the TBC coating ³²⁹ has relevance toward structural reactive material applications. ³³⁰ This study reveals a dramatic change in thermal transport ³³¹ properties associated with Al:Zr substrates that occur at ³³² elevated temperatures. Thermal properties (conductivity and ³³³ diffusivity) decrease 75–80% between 400 and 500 °C, which ³³⁴ coincides with Al₂O₃ and ZrO₂ formation on the outer surface ³³⁵ of the substrate. Slicing the substrate using a FIB with SEM- ³³⁶ EDX analysis confirms the localized formation of oxide species ³³⁷

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Figure 10. XRD patterns with peaks labeled for powders heated to 600 °C then cooled (red curve) and for powders heated to 1000 °C then cooled (blue curve) according to Figure 5. Patterns are vertically displaced for ease of comparison.



Figure 11. Thermal conductivity of various Al and Zr species as a function of temperature. Data from refs 9-11.

338 on the outer 20 μ m surface. Additional thermal analysis using 339 DSC-TGA shows intermetallic reactions are dominant, but 340 oxidation reactions can occur throughout the 400–500 °C 341 heating cycle. The formation of intermetallic and ceramic 342 species may create a duplex-type system reminiscent of 343 traditional TBCs, albeit formed in situ at moderately elevated 344 temperature rather than spray deposition or laser processing a 345 multilayer surface coating. All results show that a composite 346 metallic material can be designed to produce a dramatic 347 change in thermal transport properties at elevated temperature 348 by manipulating surface oxidation reactions that affect thermal 349 transport.

350 ASSOCIATED CONTENT

351 **Supporting Information**

352 The Supporting Information is available free of charge at 353 https://pubs.acs.org/doi/10.1021/acsami.1c02792.

SEM images and X-ray mapping of 40 μ m × 20 and 30 μ m × 15 μ m upper left side portions of entire "window" from FIB-SEM analysis of heated HIP-processed pellet (PDF)

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Notes	382

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